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METALS AND METALLIC COMPOUNDS

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IN FOUR VOLUMES

VOLUME II

METALS OF THE "A" GROUPS

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PREFACE

During the past few years so much fruitful research work has been carried out in metallography, crystallography, electrochemistry, colloid chemistry, and geo-chemistry that we are enabled to approach the subject of metals in an altogether new spirit. It is now possible to suggest reasons for phenomena which at one time appeared inexplicable, and to detect regularities where once the facts seemed chaotic. Advantage should surely be taken of the new aspect of the subject in the textbooks. The traditional practice of giving long "catalogues of salts" and empirical accounts of metallurgical processes, is no doubt of use for books of reference. But in books intended for continuous reading, such a method is far too uninspiring, and should be abandoned now that knowledge has advanced sufficiently to offer something better.

In this book, an attempt is made to correlate cause and effect, and to introduce such theoretical views as will serve to connect the known facts in an ordered and elegant sequence. The book is intended for the advanced student of inorganic and metallurgical chemistry, and for those engaged in research in these subjects. The industrial chemist will, I hope, also find it of assistance, whilst certain portions (e.g. those dealing with work-hardening, recrystallization, the effect of impurities on metals, and corrosion) should prove useful to the engineer.

The difficulties which I have experienced in writing the book have served to convince me that the work is really needed. Much information which I regard as being of the greatest importance I have found scattered through the recent volumes of the scientific and technical journals—in many cases in journals which are not commonly considered as being devoted to chemistry at all, and which appear sometimes to have escaped the notice of the writers of standard chemical textbooks.

Of the four volumes, the first is of a generalized character. It begins with an Introduction in which I have endeavoured to condense the elementary principles of general chemistry, physics and geology, a knowledge of which the reader is assumed in the body of the work to possess. The body of Volume I is divided into two parts, "The Study of the Metallic State" (Metallography) and "The Study of the Ionic State" (Electrochemistry). The metallographic portion includes the effects of deformation, annealing and alloying on the properties of metals; the electrochemical portion includes such subjects as the structure of precipitates, the colloidal state, electro-deposition and corrosion; it closes with a chapter on radioactivity. By the treatment of the metallography and electrochemistry of metals in a general fashion, with examples chosen from individual metals, these two subjects are presented in a more satisfactory manner than if they were introduced piecemeal in the sections devoted to the different metals. In addition, a great deal of wearisome repetition is avoided in the subsequent volumes.

The chapters dealing with electrochemistry have presented special difficulties. I do not believe it possible to obtain a proper understanding of the chemistry of metals without some knowledge of electrochemistry and colloid chemistry. In order to throw open these subjects to all, I have made the treatment, as far as possible, non-mathematical. A great obstacle to the attractive presentation of electrochemical principles is the barbarous character of the nomenclature in use; I have not felt justified in introducing a new nomenclature, but have tried to make the best of the existing terms, selecting a terminology which will be definite, even if it is not dignified.

In Volumes II, III and IV, I deal one by one with the individual metals. The order observed is based upon the Periodic Table in a form similar to that made popular by Sir James Walker. The old form of the Periodic Table which classes sodium along with copper has now—it is to be hoped—few active supporters, although it still ornaments the walls of our lecture theatres, and appears to find favour with the authors of chemical treatises based upon the classical model. In the new table, which accords well with the chemical and electrochemical properties of the elements and is in harmony with modern ideas of the structure of the atom, the elements can be divided into three main classes, and I have allocated a different volume to each class. Volume II deals with the metals of the "A Groups," Volume III with the "Transition Elements" ("Group VIII" of the old table), whilst Volume IV deals with the metals of the "B Groups."

The space devoted to each metal is divided into three main sections. The first deals with the metal and its compounds from the point of view of the academical laboratory. The pure chemistry of the metal and its compounds is here discussed; no reference to ores, technical processes and industrial application is made in this section, which is therefore fairly concise. The section ends with a summary of the methods of analysis of the metal in question, although the book is not intended as a practical analytical handbook.

The second section deals shortly with the terrestrial occurrence of the metal in question, starting with its origin in the rock-magma, and discussing the probable mode of formation of the important ores and minerals, both primary and secondary.

The third section—which is often the longest—is of a technical character. We start with the ore or mineral, and follow the metal through the processes of concentration and smelting, and finally consider the practical uses of the element, and of compounds containing it; I have tried to show why the properties of the individual metal—as stated in the theoretical section—render it suitable for the various uses to which it is put, and to make the technical section a correct survey of industry carried on at the present time; I have only referred to obsolete methods of procedure in a few places where such a reference is thought to be instructive.

Stress has been laid on the important points, which have been illustrated by a few chosen examples in order to avoid burdening the reader with a mass of names and numbers, which he will not retain, and which can be looked up when required in a table of physical constants or in a detailed book of reference. Proper names have largely been concentrated in the footnotes, and thus kept out of the text; I have written a book about chemistry—not about chemists. Likewise the figures are frankly diagrammatic, drawn to emphasize the salient points; in the diagrams of technical plants much that is of merely structural importance is omitted. I have only employed the historical order of description where it happens also to be the logical order.

Throughout the book numerous references are given, in footnotes, to scientific and technical literature; these should be consulted by the reader who wishes to study any given part of the subject in greater detail. In selecting these references, I have not given preference to the work of the actual originators of the various theories or processes, but have sought rather to provide the reader with the most recent information regarding the matter under discussion. The recent papers themselves will include references to the earlier ones, whilst the converse is clearly not true.

In subjects regarding which disagreement prevails at present, I have in most cases departed from the usual custom of giving in turn a summary of the views advanced by the various disputants, as this practice is apt to leave the reader hopelessly bewildered. Rather, I have endeavoured to suggest a standpoint which the average reader may safely adopt as a working hypothesis, until further research finally decides the question under dispute. If, however, the subject happens to be one of special interest to the reader, he should consult the references in the foot-notes, and form his own opinions. In these foot-notes, he will find references to many authorities whose views are not held by the present writer.

As already stated, great efforts have been made to render the book as "up-to-date" as possible, but I have not concealed the fact that uncertainty still prevails on many parts of the subject, and that research is continually being conducted to settle these doubtful points. I have endeavoured to prepare the reader to revise his own opinions without undue reluctance every time he may open a scientific journal.

I wish to return thanks to the numerous friends who have very kindly given information or advice. Especially would I mention Mr. C. T. Heycock, Dr. E. K. Rideal, Prof. H. C. H. Carpenter, and Mr. Maurice Cook. Mr. Cook has prepared the micro-photographs accompanying Volumes I, III and IV of the book, and has shown much skill and patience in obtaining results which illustrate clearly the points described in the text.

U. R. E.

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LIST OF JOURNALS REFERRED TO IN VOLUME II AND ABBREVIATIONS EMPLOYED

Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Amer. Machinist	American Machinist.
Analyst	Analyst.
Ann. Chim. Anal.	Annales de Chimie Analytique.
Ann. Chim. App.	Annali di Chimica applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Phys.	Annalen der Physik.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Board of Trade J.	Board of Trade Journal.
Boll. Chim. Farm.	Bolletino Chimico Farmaceutico.
Brit. Assoc. Report	British Association for the Advancement of Science, Report.
Bull. Soc. Chim.	Bulletin de la Société chimique de France.
Bull. Soc. d'enc.	Bulletin de la Société d'encouragement pour l'Industrie Nationale.
Bull. Amer. Inst. Min. Eng.	Bulletin of the American Institute of Mining (and Metallurgical) Engineers.
Canadian Geol. Surv. Mem.	Canadian Geological Survey, Memoirs.
Carn. Schol. Mem.	Carnegie Scholarship Memoirs (Iron and Steel Institute).
Chem. Drug.	Chemist and Druggist.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker-Zeitung.
Chim. et Ind.	Chimie et Industrie.
Comptes Rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Discovery	Discovery.
Econ. Geol	Economic Geology.
Electrician	Electrician.
Electrochem. Ind.	Electrochemical Industry.
Electrotech. Zeitsch.	Elektrotechnische Zeitschrift.
Engineering	Engineering.
Eng. Min. J.	Engineering and Mining Journal.
Gazetta	Gazetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Int. Cong. App. Chem.	International Congress of Applied Chemistry.

LIST OF JOURNALS.

Iron Age	Iron Age.
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Inst. Met.	Journal of the American Institute of Metals.
J. Chem. Ind., Tokyo	Journal of Chemical Industry, Tokyo.
J. Chem. Met. Min. Soc., S. Africa	Journal of the Chemical, Metallurgical and Mining Society of South Africa.
J. Chem. Soc.	Journal of the Chemical Society.
J. Coll. Sci. Tokyo	Journal of the College of Science, Tokyo Imperial University.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Geol.	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Met.	Journal of the Institute of Metals.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Prakt. Chem.	Journal für praktische Chemie.
J. Röntgen Soc.	Journal of the Röntgen Society.
J. Roy. Soc. Arts	Journal of the Royal Society of Arts.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Wash. Acad. Sci.	Journal of the Washington Academy of Science.
Koll. Zeitsch.	Kolloid-Zeitschrift.
Lieb. Ann.	Liebig's Annalen der Chemie.
Mech. World	Mechanical World.
Met. Chem. Eng.	Metallurgical and Chemical Engineering (also called "Chemical and Metallurgical Engineering").
Met. u. Erz	Metall und Erz.
Min. Ind.	Mineral Industry.
Miss. Geol. Surv.	Missouri Geological Survey.
Mitt. Kgl. Mat. Prüfungsamt	Mittheillungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Monatsh.	Monatshefte für Chemie und verwandte Teile Anderer Wissenschaften.
Mon. Scient.	Moniteur Scientifique.
Nature	Nature.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Phil. Mag.	Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Rev.	Physical Review.
Phys. Zeitsch.	Physikalische Zeitschrift.
Proc. Amst. Acad.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.

Rec. Trav. Chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. Prod. Chim.	Revue des produits chimiques.
Sch. Min. Quart.	School of Mines Quarterly.
Soil Sci.	Soil Science.
Sprechsaal	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Svensk Kem. Tidskr.	Svenska Kemisk Tidskrift.
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining (and Metallurgical) Engineers.
Trans. Canadian Min. Inst.	Transactions of the Canadian Mining Institute.
Trans. Ceram. Soc.	Transactions of the (English) Ceramic Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. Soc. Glass Tech.	Transactions of the Society of Glass Technology.
U.S. Bur. Mines, Bull.	United States Bureau of Mines, Bulletins.
U.S. Bur. Stand. Bull.	United States Bureau of Standards, Bulletins.
U.S. Com. Rep.	United States Commerce Reports.
U.S. Dept. Agric. Bur. Chem. Bull.	United States Department of Agriculture, Bureau of Chemistry, Bulletins.
U.S. Dep. Agric., Bur. Soils, Bull.	United States Department of Agriculture, Bureau of Soils, Bulletin.
U.S. Geol. Surv., Min. Res.	United States Geological Survey, Mineral Resources.[1]
Zeitsch. Anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. Angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. Anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Metallkunde	Zeitschrift für Metallkunde.
Zeitsch. Phys.	Zeitschrift für Physik.
Zeitsch. Phys. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.

[1] The year stated is always the year of the series; the year of publication is invariably later.

GROUP IA

THE ALKALI METALS

	Atomic Weight.	Normal Electrode Potential (Hydrogen Scale).
Lithium	6·94	−3·027 volts
Sodium	23·00	−2·715 „
Potassium	39·10	−2·925 „
Rubidium	85·45	−2·928 „
Cæsium	132·81	——

The first group of elements consists of metals possessing properties very different from those which we are accustomed to associate with metals. They are all highly reactive substances, standing at the negative end of the Potential Series ; so reactive are they that they decompose water with great violence, hydrogen being produced. The heat-evolution of the reaction is so great that the hydrogen in most cases catches fire. The great reactivity with water is certainly connected, not only with the electrochemical character of the metals, but also with the solubility of the hydroxides. These are well-defined compounds of most pronounced basic character. They lose their combined water only with the greatest difficulty, and it is in most cases impossible to prepare the anhydrous oxide merely by heating the hydroxide. In this respect they present a striking contrast with the so-called " hydroxides " of the heavy metals, in which the water appears to be very loosely combined. The dissolution of the oxide or hydroxide in acids is attended by great evolution of heat, a fact which illustrates the strong basicity of the compounds. Another distinguishing feature of the group, due to the same cause, is that the oxides cannot—with the exception of lithium oxide—be prepared by heating the nitrate or carbonate ; the acid constituent of these salts is too firmly fixed. The salts are mostly very well-defined crystalline bodies. The normal salts of strong acids are practically unhydrolysed and generally react neutral to ordinary indicators. The salts are in almost every case without colour, except where they are derived from a coloured acid. Another noteworthy fact is that—with a few unimportant exceptions—all the salts are freely soluble in water.

There is in each case only one class of stable compounds, in which the metal is monovalent; peroxides and polysulphides are known, but these are comparatively unstable substances, and behave as though part of the oxygen or sulphur were loosely attached.

It is noteworthy that lithium, the lowest member of the group, differs in several respects from all the others, and has certain points of resemblance to the metals of the succeeding Group IIA. It is chemically less reactive than the other metals, although, curiously enough, it appears to have a distinctly more negative electrode potential than the other elements—an anomaly which seems to require an explanation.

LITHIUM

Atomic Weight 6·94

The Metal

Freshly prepared lithium is a metal displaying a bright silvery lustre, but the surface quickly tarnishes when exposed to a damp atmosphere. It is the lightest solid known, the specific gravity being about 0·534. The metal is softer than lead, although harder than the other members of Group IA. It melts at 186° C.

Lithium is the least reactive metal of the group, but nevertheless it decomposes water readily. When a piece of lithium is thrown on to water, it floats on the surface, hydrogen being freely evolved; lithium hydroxide is formed in the solution, which acquires an alkaline reaction. The heat generated by the change is, however, not so great as to cause the ignition of the hydrogen or even to melt the lithium. Needless to say, the metal also evolves hydrogen from dilute acids.

As has been stated, the metal quickly tarnishes in damp air, although it is unaffected by dry air at ordinary temperatures. When heated in air, lithium first melts, and then takes fire, burning with a bright white flame, and forming lithium oxide. The brightness of the flame is no doubt due to particles of incandescent lithium oxide.

Laboratory Preparation. The metal can be prepared by the electrolysis of the fused chloride, but it is more convenient to use a mixture of the bromide and chloride, as such a mixture melts at a lower temperature. The mixture, containing 85 per cent. of bromide, is fused in a copper pot. A carbon rod anode, and two iron wires, which serve as cathodes, are introduced, and are joined to a battery giving an E.M.F. of 10 volts. Shining beads of lithium soon appear at the cathodes, and may be removed from time to time with an iron ladle.[1]

Since the metal decomposes water, it is useless to try and prepare it by the electrolysis of an aqueous solution of a salt, but when a solution of lithium chloride in pyridine is electrolysed, the metal is produced as a silvery coating upon the cathode.[2]

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[1] O. Ruff and O. Johannsen, *Zeitsch. Elektrochem.* **12** (1906), 186.

[2] L. Kahlenberg, *J. Phys. Chem.* **3** (1899), 602.

Compounds

Lithium oxide, Li_2O, is formed when the metal is burnt in air. Unlike the oxides of the other alkali metals, it may also be formed by heating the nitrate. This fact shows that lithium oxide is less basic than the oxides of the other metals. It is best obtained in a state of purity [1] by heating the carbonate in a current of hydrogen at 780-800° C. The pure oxide is a white substance. It combines with water far less readily than the oxides of potassium and sodium, another circumstance quite in keeping with the less active character of lithium. It does, however, slowly enter into combination with water, forming the **hydroxide**, LiOH, a soluble white crystalline substance; the aqueous solution shows an alkaline reaction and caustic properties, and slowly absorbs carbon dioxide from the air, forming lithium carbonate.

Salts. Most of the lithium salts are soluble, colourless, crystalline bodies. They may be formed by the action of the acid in question upon lithium hydroxide or carbonate, the solution produced being afterwards evaporated. The **chloride**, LiCl, crystallizes in octahedra, and is very soluble in water and also in alcohol; it is deliquescent, and forms various hydrates. The **nitrate** and **sulphate** are also soluble crystalline solids.

The **carbonate**, Li_2CO_3, is less soluble than those of the other alkali metals. It can in fact be obtained as a crystalline precipitate through the addition of ammonium carbonate to a concentrated solution of lithium chloride, but no precipitate is formed when the solution is dilute. It is more soluble in water containing carbon dioxide, for under these circumstances, the acid carbonate, $LiHCO_3$, is formed in the solution.

Lithium Phosphate, Li_3PO_4, is an important insoluble salt of lithium, and is obtained as a precipitate upon the addition of sodium phosphate to a lithium salt solution, preferably made alkaline with ammonia. The solubility limit in water is about 1 part in 2,500 at ordinary temperatures. It is, however, soluble in dilute acids, and, by crystallization of the solution in nitric acid, a soluble **acid phosphate**, LiH_2PO_4, is obtained.

In the solubility relations of its salts, lithium forms a link between the other alkali metals, which have very soluble phosphates and carbonates, and the metals of the succeeding groups in which the phosphates and carbonates are insoluble.

Lithium peroxide is precipitated when hydrogen peroxide and alcohol are added to a solution of the hydroxide. The white crystals which appear in the solution contain water and hydrogen peroxide in combination, but yield the anhydrous peroxide (usually written Li_2O_2), when allowed to stand over phosphorus pentoxide for some weeks.[1]

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[1] de Forcrand, *Comptes Rend.* **144** (1907), 1402.

Analytical

Most lithium compounds, moistened with hydrochloric acid and introduced into the Bunsen flame, impart a red colour to the flame. On examining the light from the flame through a spectroscope, a bright red line and a weaker yellow line may be seen. Very minute traces of lithium can be detected by means of the spectroscope, even in the presence of other metals.

The analytical separation of lithium from the metals of succeeding groups depends on the fact that most of the latter have insoluble hydroxides (and can therefore be precipitated with calcium hydroxide), or have insoluble carbonates (and can therefore be precipitated with ammonium carbonate, in the presence of ammonia). In both cases, if the solution is not too concentrated, the lithium remains in solution.

The separation of lithium from members of its own group, which also have soluble hydroxides and carbonates, depends on the fact that lithium chloride is soluble in amyl alcohol, whilst the chlorides of sodium and potassium are precipitated when amyl alcohol is added to a concentrated aqueous solution, and can be separated by filtering the liquid. The filtrate containing lithium chloride can be evaporated and converted, by heating with sulphuric acid, to lithium sulphate, in which form the lithium may be weighed.[2]

The method just described is not exact, because the precipitation of potassium and sodium is not quite complete; for accurate work, it is necessary to make a small deduction from the weight of so-called lithium sulphate found, on account of the small amount of sodium or potassium sulphate which it necessarily contains.

Amyl alcohol is an unpleasant substance to work with, on account of the odour and the physiological action of the vapour. Other methods have been worked out depending upon the solubility of lithium chloride in other solvents, such as isobutyl alcohol,[3] or an ether-alcohol mixture[4]; in each case sodium and potassium chlorides are nearly insoluble in the liquid in question.

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[1] de Forcrand, *Comptes Rend.* **130** (1900), 1465.

[2] W. W. Skinner and W. D. Collins, *U.S. Dept. Agric., Bur. Chem., Bull.* **153** (1912).

[3] L. W. Winkler, *Zeitsch. Anal. Chem.* **52** (1913), 628.

[4] S. Palkin, *J. Amer. Chem. Soc.* **38** (1916), 2326.

TERRESTRIAL OCCURRENCE

Lithium is one of the less common elements occurring in rock magma, and, during the solidification of an igneous intrusion, tends to become concentrated in the acidic portions which are the last to solidify. Thus granite contains more lithium than do the basic rocks, whilst the pegmatite veins which represent absolutely the last portions of a granitic magma to solidify are often comparatively rich in lithium minerals. Lithium compounds appear to have been given off in the vaporous form during the final stage of consolidation, and many of the minerals found in the neighbourhood of igneous rocks seem to have a pneumatolytic origin. Also the thermal waters given off by igneous intrusions contain an appreciable amount of lithium, which consequently appears in many mineral springs, notably those of Baden Baden; the medicinal value of such springs is no doubt largely due to this element.

The main lithium-bearing minerals occurring in granitic rocks and pegmatite veins are the silicates :—

Lepidolite (lithia mica) . .	$LiK[Al(OH,F)_2]Al(SiO_3)_3$
Spodumene	$LiAl(SiO_3)_2$
Petallite	$LiAl(Si_2O_5)_2$

Often associated with spodumene are the phosphates :—

Amphlygonite . . .	$Li(AlF)PO_4$
Triphylite	$Li(Fe,Mn)PO_4$

Lithium minerals are often associated with the ores of tin, another metal of which the ores appear frequently to have a pneumatolytic origin. The tin ores of the Black Hills, S. Dakota, are famous for their enormous crystals of spodumene; one particular crystal has a face over 42 feet long, whilst crystals 30 feet long are comparatively common.

By the weathering of rocks containing lithium, or by the influx of waters originating in mineral springs, traces of lithium are usually found in ordinary river water and consequently in the sea. Moreover, since land plants and also seaweed have the power of absorbing the element, minute traces of lithium are to be found in almost all vegetable products; ordinary tobacco ash, for instance, contains an appreciable quantity of lithium, a fact which chemists who are searching for traces of the element in other materials will do well to remember.

In short, lithium is a very widely distributed element, although present usually only in small quantities.

LITHIUM

TECHNOLOGY AND USES

The most convenient minerals to utilize as the source of lithium are lepidolite (lithia-mica) or spodumene; the former mineral is largely mined in California, and the latter in South Dakota.[1]

Like other silicate minerals, they are insoluble in water, and, in the form in which they occur in rocks, are often only slowly attacked by acids. If, however, the lithium mineral is fused, and then poured into cold water, the rapid cooling usually renders the mass brittle, and it can readily be reduced to a fine powder which, on account of the large surface presented, is fairly rapidly decomposed by hot, concentrated sulphuric acid. After digestion with this acid, the mass, whilst still hot, is extracted with water, and filtered to separate the silica; the filtrate contains the sulphates of all the metals present in the original mineral, the most important being aluminium, potassium, magnesium and lithium.

By adding potassium sulphate to the boiling liquid, most of the aluminium is thrown down as the rather sparingly soluble double salt, alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$); the rest of the aluminium is precipitated as hydroxide by the addition of calcium hydroxide. The sulphates remaining in the filtered liquid are converted to chlorides by the addition of barium chloride, and the liquid is again filtered to separate barium sulphate; it is then evaporated to dryness.

Of the chlorides present, only the chlorides of calcium and lithium are appreciably soluble in alcohol, and can therefore be extracted with that solvent. The calcium can afterwards be precipitated by ammonium oxalate as the insoluble calcium oxalate, leaving lithium—nearly free from other metals—in the solution. From the chloride, other salts of lithium can be prepared.

In an alternative process, which was worked out in America, the use of alcohol is dispensed with. After the removal of the aluminium, the solution containing sulphates of lithium, calcium and other metals is treated with ammonia and ammonium oxalate to remove calcium, and the lithium is then precipitated from the filtrate as carbonate, by the addition of potassium carbonate.[2]

Uses of Lithium Salts. Various salts of lithium are used for medicinal purposes, being found useful in all ailments—such as gout and arthritis—which are connected with the presence of uric acid in the system. It happens that lithium urate is more soluble than the other salts of uric acid, and it is commonly stated that the beneficial action of lithium salts depends on that fact; doubt has been expressed, however, as to whether this explanation is correct. The use of lithium salts in medicine has, however, declined somewhat owing to the introduction of organic drugs. Apart from natural mineral waters containing lithium, "lithia water" (a water containing lithium bicarbonate and aerated with carbon dioxide) is manufactured on a considerable scale; lithium is often introduced into medicine as the carbonate, whilst the salicylate and the acetylsalicylate are also produced, especially on the Continent, for medical purposes.

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[1] H. Insley, *U.S. Geol. Surv., Min. Res.* (1919), II., 37.

[2] W. J. Schieffelin and T. W. Cappon, *J. Soc. Chem. Ind.* 27 (1908), 549.

Lithium hydroxide is employed in the nickel accumulator, whilst lithium compounds have a limited use in the manufacture of certain glasses and glazes, their apparent function being to reduce the viscosity.

SODIUM

Atomic weight 23·00

The Metal

Sodium resembles lithium in physical properties. It is a white metal possessing a silvery lustre, but tarnishes very readily in ordinary air. It is lighter than water, although distinctly heavier than lithium ; the specific gravity is 0·971. It is very soft and can readily be pressed into the form of wire or ribbon by extrusion through an orifice at the ordinary temperature. It becomes softer still as the temperature rises, and melts at 97° C.

The metal boils at 877·5°. When light is allowed to pass through a long column of sodium vapour, it emerges slightly bluish in colour.[1] On the other hand, when sodium vapour is itself heated, it emits yellow light, of wave-lengths $5{,}896 \times 10^{-8}$ cm. and $5{,}890 \times 10^{-8}$ cm., corresponding to the so-called D-line (or D-pair) of the solar spectrum. The yellow colour produced when traces of a sodium compound are introduced into a non-luminous flame is due to this cause. It is interesting to note that, at temperatures far below those at which it normally becomes luminous, the vapour, when exposed to an intense light coming from a flame containing sodium, shows a yellow fluorescence, emitting light of the characteristic wave-lengths by "resonance." Moreover, if the "exciting light" contains one line of the pair only, consisting entirely of wave-length $5{,}890 \times 10^{-8}$ cm., the light given off by the vapour consists of this one wave-length only, the line corresponding to $5{,}896 \times 10^{-8}$ cm., being entirely absent.[2] When exposed to white light, sodium vapour also gives off rays of many other wave-lengths, and the resultant fluorescence is green.

Sodium is more reactive than lithium. It evolves hydrogen with considerable violence when brought into contact with water, sodium hydroxide being formed. A fragment of sodium floating on the surface of water is caused to dart about owing to the generation of the hydrogen bubbles, and so the heat evolved is distributed over the water. But, if the motion of the fragment be impeded, the temperature becomes locally so high that the hydrogen catches fire.

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[1] H. E. Roscoe and A. Schuster, *Proc. Roy. Soc.* **22** (1874), 362.

[2] R. W Wood, *Phil. Mag.* **10** (1905), 513 : R. W. Wood and L. Dunoyer, *Phil. Mag.* **27** (1914), 1018, 1025.

Sodium is readily oxidized if exposed to damp air. When heated, it burns readily with a yellow flame forming a mixture of oxides.

Laboratory Preparation. The metal can be made from its compounds in more than one way. It can be prepared from the hydroxide by heating it with carbon, but, since the reaction is highly endothermic, a high temperature is needed for the reduction. A more convenient means of supplying the energy needed is provided by the electrolytic method. For demonstrating the formation on a small scale, the original method employed in 1807 by Davy, the discoverer of sodium, can be adapted. A small stick of damp sodium hydroxide is placed in a platinum dish joined to the negative pole of a 100 volt main. A platinum wire joined (through a fuse) to the positive wire of the main is used as anode, and is brought into contact with the upper part of the stick. The sodium hydroxide melts, and after a short time globules of sodium appear on the dish cathode. If it is desired to prepare sodium in the laboratory on any considerable scale, it is best to imitate as closely as possible the technical method, described in the technical section.

It is clearly impossible to deposit metallic sodium electrolytically from aqueous solution. If, however, a concentrated solution of sodium hydroxide is electrolysed with a mercury cathode, a sodium-mercury alloy (sodium amalgam) is obtained. Having prepared the amalgam, it is possible to drive off the mercury by distillation in an atmosphere of petroleum, metallic sodium being thus obtained. Sodium amalgam is further described below.

Compounds

Sodium hydroxide, NaOH, is formed when sodium reacts with water. On evaporating the solution, the fused hydroxide is left, and solidifies on cooling. It can be obtained from sodium carbonate by the action of calcium hydroxide (slaked lime), which when mixed with a sodium carbonate solution, produces sodium hydroxide and calcium carbonate

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

The reaction depends upon the fact that calcium carbonate is less soluble than calcium hydroxide. By filtering off the precipitate of calcium carbonate, a solution of sodium hydroxide, still mixed with some sodium carbonate, is obtained.

The hydroxide, usually known as "caustic soda," is a white solid, which melts at 310° C. It does not lose its water of combination on heating. On exposure to damp air, it readily takes up more water, becoming moist on the surface, and absorbing carbon dioxide, if present, also. It is very soluble in water, and evolves much heat when it dissolves. The solution, which is strongly alkaline, also readily absorbs carbon dioxide. Sodium hydroxide dissolves in alcohol, and, for that reason, the material prepared from sodium carbonate can be purified from any traces of the carbonate which may still remain mixed with it. The impure caustic soda is extracted with alcohol, which dissolves the hydroxide but not the carbonate, and a pure hydroxide is obtained upon evaporating the filtered solution.

Sodium oxide, Na_2O, is the anhydride of $NaOH$, but cannot be made by heating the latter. Nor is it possible to obtain such a strongly basic oxide by heating the nitrate or carbonate. It can be prepared, however, by the action of sodium on the fused hydroxide. It is also formed by burning sodium in a limited supply of oxygen at a low temperature, but usually, especially if the temperature becomes unduly elevated, the peroxide is produced along with it. As commonly prepared, it is a greyish substance, but when quite pure it is said to be white. Sodium oxide reacts with great violence with water, the hydroxide being formed.

Sodium Salts. Sodium is unique among the metals in that the salts—almost without exception—are readily soluble. They are mostly well-defined, colourless, crystalline bodies, and are conveniently obtained by the action of the respective acids upon sodium hydroxide, or, if preferred, sodium carbonate.

Sodium chloride (*common salt*), $NaCl$, forms colourless cubic crystals possessing cubic cleavage. Unlike lithium chloride, it is not visibly deliquescent, when pure, although it absorbs, from damp air, enough water to cause a sensible increase in weight. It is very soluble in water, 100 grams of water dissolving 36 parts of salt; the solubility is almost independent of the temperature. When concentrated hydrochloric acid is added to a solution of sodium chloride, the salt is thrown out of solution as a crystalline precipitate; advantage is taken of this fact in the method of preparing sodium chloride free from impurities.

Sodium chloride is practically insoluble in alcohol.

Sodium nitrate, $NaNO_3$, is another very soluble salt of sodium, crystallizing in colourless rhombohedra. Unlike the nitrates of the heavy metals, it does not yield the oxide at high temperatures. It merely evolves oxygen, when heated, leaving the nitrite

$$2NaNO_3 = 2NaNO_2 + O_2.$$

Sodium nitrite ($NaNO_2$) is obtained in a purer state by treating silver nitrite with sodium chloride; the filtrate from the precipitated silver chloride yields sodium nitrite upon evaporation. The salt is white, deliquescent and very soluble. The solutions display both oxidizing and reducing properties, under different circumstances.

Sodium sulphate, Na_2SO_4, is obtained when sodium hydroxide is neutralized with sulphuric acid. If the solution produced be evaporated above 33° C., the anhydrous salt is obtained in rhombic crystals, isomorphous with silver sulphate; if the crystallization takes place below 33° C., the decahydrate $Na_2SO_4.10H_2O$ is usually formed in monoclinic crystals (*Glauber's Salt*). A glance at Fig. 1 will show the reason for this. Below 33° C., the decahydrate, the solubility of which is shown by the curve AB, is less soluble than the anhydrous salt; above 33° C., as shown by the curve CD, the anhydrous salt is the less soluble, and will generally be deposited.

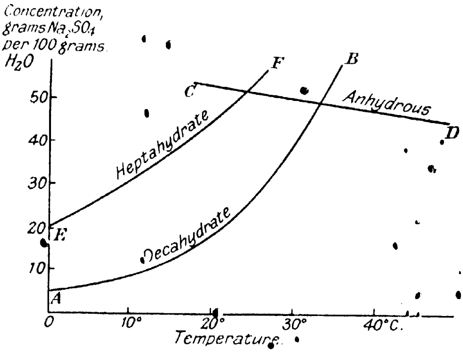

FIG. 1.—Solubility Curves of Sodium Sulphate.

It should, however, be noticed that supersaturation of the solution readily occurs. If a saturated solution of sodium sulphate be prepared at a high temperature, it may be cooled in a clean flask (carefully covered over to prevent the admission of dust or any nuclei which would start the crystallization of $Na_2SO_4.10H_2O$) to quite low temperatures without the commencement of crystallization, although the concentration far exceeds the "solubility limit" of the decahydrate. In fact even when, at a very low temperature, usually between 6° C. and −13° C., spontaneous crystallization does set in, it is not the decahydrate but a heptahydrate ($Na_2SO_4.7H_2O$) which is generally formed. The heptahydrate, the solubility limits of which are shown by curve EF, is at all temperatures more soluble than the decahydrate, and is therefore always "metastable," and can only be obtained from a solution distinctly supersaturated with the decahydrate. Crystals of the decahydrate, when exposed to the air, "effloresce"; that is, they lose water, falling to a white powder consisting mainly of the anhydrous salt.

When twice the quantity of sulphuric acid needed for neutralization is added to sodium hydroxide, sodium hydrogen sulphate or **sodium bisulphate**, $NaHSO_4$, is obtained; on heating the latter at 250–270°, it loses water, **sodium pyrosulphate**, $Na_2S_2O_7$, being produced.

Of the **sulphites**, **sodium bisulphite**, $NaHSO_3$, is obtained when a caustic soda solution is saturated with sulphur dioxide. If an equal quantity of caustic soda to that originally used be then added to the liquid, the **normal sulphite**, Na_2SO_3, is produced, and can be isolated in prisms containing seven molecules of water by evaporation of the solution. The solution, heated with sulphur, yields the important salt, **sodium thiosulphate**, $Na_2S_2O_3$, which may be obtained, on crystallization, in transparent monoclinic crystals containing five molecules of water. The solution is fairly stable when neutral, but, on the addition of acid, is decomposed, sulphur being regenerated as a fine precipitate. Sodium thiosulphate is a reducing agent, and reacts with iodine according to the equation

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

a reaction largely used in volumetric analysis for the estimation of iodine, and, indirectly, of other oxidizing agents. The product of oxidation, sodium tetrathionate ($Na_2S_4O_6$), is of no special interest, and is rarely isolated, being somewhat unstable in the solid state.

The two **sulphides**, Na_2S and $NaHS$, are prepared in solution in an analogous manner to the sulphites, sulphuretted hydrogen gas being used instead of sulphur dioxide.

Sodium carbonate, Na_2CO_3, is formed when a boiling solution of caustic soda is saturated with carbon dioxide, and the solution crystallized. If the crystallization takes place below 31·8° C., the **decahydrate** (*washing soda*), $Na_2CO_3.10H_2O$, is formed in transparent crystals; whilst on evaporation at high temperatures, a monohydrate $Na_2CO_3.H_2O$ is the normal product. Over a narrow range of temperature (namely 31·8 to 36° C.), a heptahydrate, $Na_2CO_3.7H_2O$, is the stable phase, and it is not infrequently deposited from supersaturated solutions even outside these limits; there are two separate crystalline forms of this hydrate. All the hydrates give anhydrous Na_2CO_3 on heating.

Sodium carbonate is, unlike lithium carbonate, quite soluble in water. The solution is to some extent hydrolysed, and reacts alkaline to nearly all indicators; for carbonic acid is only a weak acid, whilst caustic soda is a powerful alkali.

Sodium bicarbonate, $NaHCO_3$, is formed when sodium hydroxide solution is saturated with carbon dioxide at the ordinary temperature. The solution gives off carbon dioxide when boiled, the normal carbonate being left behind, and the same change occurs if the solid bicarbonate is heated. The bicarbonate, although distinctly alkaline to methyl orange, is very nearly neutral to phenolphthalein. In fact, if the solution is cooled down to 0°, so as to reduce the hydrolysis, it is said to be absolutely neutral to that indicator.

Sodium Phosphates. A large number of sodium phosphates are known. They are derived from the three phosphoric acids by the replacement of different numbers of hydrogen atoms with sodium.

(1) The three **orthophosphates,** Na_3PO_4, Na_2HPO_4 and NaH_2PO_4 are formed by the action of phosphoric acid on the requisite quantity of caustic soda; various hydrates are known. The "*common sodium phosphate*" is $Na_2HPO_4.12H_2O$, and can readily be obtained in large monoclinic crystals; the solution has an alkaline reaction, for phosphoric acid is but a weak acid. All the sodium orthophosphates give a yellow precipitate with silver nitrate; they are all freely soluble in water, in contrast to those of lithium, and of most of the heavier metals.

(2) Sodium **pyrophosphate,** $Na_4P_2O_7$, is formed when common sodium phosphate is heated.

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

It is soluble in water, the solution giving a white precipitate with silver nitrate.

(3) Sodium **metaphosphate,** $NaPO_3$, is formed by strongly heating sodium dihydrogen orthophosphate

$$NaH_2PO_4 = NaPO_3 + H_2O$$

or sodium ammonium hydrogen phosphate (microcosmic salt)

$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O.$$

Very many forms—prepared under different conditions—have been described,[1] and various formulæ such as $NaPO_3$, $(NaPO_3)_2$, $(NaPO_3)_3$, $(NaPO_3)_4$ and $(NaPO_3)_6$, have been assigned to them by different investigators, often on very slender evidence. There seems very little doubt, however, but that some of the different forms described are distinct chemical individuals, differing amongst themselves as regards solubility and the conductivity of the solutions. But the question is complicated by the possibility that many of the forms described are solid solutions, and probably in some cases contain pyrophosphates or orthophosphates; some of the forms described may be partially devitrified glasses. The whole experimental work requires to be repeated, and the results ought then to be reviewed afresh in the light of modern knowledge regarding the character of crystals and of solutions.

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[1] G. Tammann, *Zeitsch. Phys. Chem.* **6** (1890), 122; G. von Knorre, *Zeitsch. Anorg. Chem.* **24** (1900), 369; F. Warschauer, *Zeitsch. Anorg. Chem.* **36** (1903), 13[illegible].

Sodium borate. Although boron trioxide is but a feebly acidic oxide, it is very non-volatile. In consequence it is possible to convert almost any sodium salt to a borate by heating with boron trioxide at a sufficiently high temperature. Even sodium sulphate when heated with boron trioxide at a very high temperature loses sulphur trioxide, sodium borate being left. The borates are more conveniently prepared by acting upon sodium hydroxide solution with boric acid or by fusing the hydroxide with boron trioxide. The best-known member of the group is **borax,** $Na_2B_4O_7$, which may be obtained by crystallization from solutions below 60° in transparent monoclinic prisms containing ten molecules of water; at higher temperatures, a pentahydrate is obtained. Solutions of borax are strongly alkaline, owing to hydrolysis. Anhydrous borax is formed as a transparent glass when one of the hydrates is heated; the mass swells up in a curious way while the water is being given off, and finally settles down to form molten anhydrous borax. This has a power of dissolving the oxides of the heavier metals, small traces of which are capable of giving a marked colour to the glass; it is sometimes stated that the oxides exist as colloid particles in the borax, but probably, in most cases, the colour may be regarded as due to the presence of a borate of the metal added.

Sodium silicates are formed by fusing caustic soda with silica. Compounds such as Na_4SiO_4, Na_2SiO_3, and $Na_2Si_2O_5$ have been described, and some at least of these can be produced as definite crystals of uniform composition; but many of the so-called "silicates" described by different observers are glassy masses, the composition of which is only determined by the proportions in which the ingredients are melted together. The solutions are much hydrolysed, and react strongly alkaline; when concentrated the solutions are thick, viscous liquids. The solubility falls off as the silica-content increases. The silicates of sodium rich in silica will be further discussed in the technical section dealing with "glass."

Products of the Action of Chlorine on Sodium Hydroxide. When chlorine is passed into a well-cooled solution of caustic soda, it is absorbed, with the formation of sodium **hypochlorite** and chloride

$$Cl_2 + 2NaOH = NaCl + NaClO + H_2O.$$

If the temperature of the solution is raised, the hypochlorite itself decomposes, forming sodium **chlorate**

$$3NaClO = 2NaCl + NaClO_3.$$

If crystallized sodium chlorate be heated cautiously just above its melting-point, it becomes converted to a mixture of **perchlorate** and chloride

$$4NaClO_3 = 3NaClO_4 + NaCl$$

and finally on stronger heating of the perchlorate, the latter evolves oxygen and leaves sodium chloride alone

$$NaClO_4 = NaCl + 2O_2.$$

It ought to be pointed out that, as a matter of fact, other simultaneous changes occur along with those expressed by the simple equations given.[1] For instance, when sodium chlorate is heated, a certain amount of oxygen, as well as perchlorate, is always produced; and when the perchlorate is heated some chlorate is regenerated along with the oxygen.

As was pointed out in the section on Free Energy (Vol. I, page 87), each step of the change

$$\begin{array}{c}\text{Chlorine}\\\text{and}\\\text{Alkali}\end{array} \rightarrow \left\{\begin{array}{c}\text{Hypochlorite}\\\text{and}\\\text{Chloride}\end{array}\right. \rightarrow \left\{\begin{array}{c}\text{Chlorate}\\\text{and}\\\text{Chloride}\end{array}\right. \rightarrow \left\{\begin{array}{c}\text{Perchlorate}\\\text{and}\\\text{Chloride}\end{array}\right. \rightarrow \left\{\begin{array}{c}\text{Oxygen}\\\text{and}\\\text{Chloride}\end{array}\right.$$

involves a transformation of an unstable substance into a more stable substance. The stability of the bodies increases, and the oxidizing energy of the bodies diminishes, as we pass along the series. Sodium hypochlorite retains much of the oxidizing energy present in chlorine, and is a powerful oxidizer; it is so unstable as to be very difficult to prepare in the solid state.[2] Sodium chlorate is a much less powerful oxidizer and can easily be obtained in solid form by the crystallization of the solution, whilst the perchlorate, although possessing the highest oxygen-content, has only the feeblest oxidizing properties, and the solid requires strong heating before decomposition takes place.

The formation of hypochlorites, chlorates and perchlorates is further described in the sections devoted to the technology of sodium and potassium.

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[1] J. Scobai, *Zeitsch. Phys. Chem.* 44 (1903), 319.

[2] For details of method for preparing sodium hypochlorite in crystalline form, see R. P. Applebey, *Trans. Chem. Soc.* 115 (1919), 1106.

Almost the only sparingly soluble salt of sodium is the **dihydroxytartrate**, which is precipitated when a cold sodium salt solution is treated with a saturated solution of potassium dihydroxytartrate.

Peroxide. When sodium is burnt in air, higher oxides are formed as well as the compound Na_2O. When the product is heated in excess of air, the sole product is the pale yellow peroxide Na_2O_2. This substance is a powerful oxidizer. The solution in water gives off oxygen gas slowly; the solution in dilute hydrochloride consists largely of hydrogen peroxide and sodium chloride, and is more stable.

It is possible that a still higher oxide Na_2O_3, exists, but its identity is a little doubtful.

Polysulphides[1] are also known. Sulphur dissolves in an aqueous solution of sodium sulphide, yielding a yellowish liquid, from which it is rather difficult to isolate any solids of definite composition. If, however, an alcoholic solution of sodium hydrogen sulphide (NaHS) be boiled with sulphur, hydrogen sulphide is evolved, and, after concentration of the solution, it is possible to obtain a yellow crystalline crust having the composition Na_2S_4. It is very hygroscopic and dissolves in water producing a deep orange solution.

When sulphur and sodium sulphide are melted together, and allowed to solidify, the mass produced consists of polysulphides. The curve showing the connection between the composition of the mass and the melting-point consists of six portions, and appears to indicate the existence of the compounds

$$Na_2S_2,\ Na_2S_3,\ Na_2S_4 \text{ and } Na_2S_5.$$

The maxima in the melting-point curve corresponding to the compounds of composition Na_2S_2 and Na_2S_4 is extremely well marked, but the existence of Na_2S_3 and Na_2S_5 is more doubtful.

A solid **hydride** of sodium is known having the composition NaH. It is obtained when a stream of hydrogen is passed over sodium heated to about 350° C.; a white fume consisting of the finely divided hydride is carried away by the gas-stream. Details of the method of preparation must be sought elsewhere.[2]

Sodium Amalgam. When sodium is added to mercury, it dissolves, great heat being evolved. After a certain amount has been added the mercury becomes viscous, and finally an alloy which is solid at ordinary temperatures is formed. In the solid amalgams various intermetallic compounds are believed to exist :—

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[1] A. Rule and J. S. Thomas, *Trans. Chem. Soc.* **105** (1914), 177; **111** (1917), 1063.

[2] F. Ephraim and E. Michel, *Helv. Chim. Acta*, **4** (1921), 762.

$$NaHg_4,\ NaHg_2,\ NaHg,\ Na_3Hg_2,\ Na_5Hg_2,\ Na_3Hg$$

One of these, $NaHg_2$, has a maximum freezing-point at about 360°, far above that of either pure metal. Our belief in the existence of these compounds depends mainly on the shape of the freezing-point curve of the alloys ; it is extremely difficult to isolate the compounds in a pure state.[1]

As stated above, it is also possible to produce a dilute sodium amalgam by electrolysing the aqueous solution of a sodium salt with a mercury cathode. Partly because the cathodic potential required to produce sodium amalgam is less negative than that required to produce pure sodium, and partly because of the high overpotential of mercury, very little current is wasted in the generation of hydrogen. Thus whilst the production of sodium itself in aqueous solution would be impossible, the production of the amalgam proceeds at high current efficiency.

For the same reasons dilute sodium amalgam is a much more stable substance than sodium itself and does not evolve hydrogen readily when brought into contact with water. The decomposition of water by the dilute amalgam is greatly aided by contact with a substance like iron or carbon having a low hydrogen-overpotential. A short-circuit cell of the type

Hg containing Na | water | iron (or carbon),

is set up, the sodium entering the ionic state and causing the production of hydrogen gas at the iron or carbon.

Dilute sodium amalgam is useful as a reducing agent in organic chemistry, its action being milder and better capable of control than that of pure sodium.

Ammonia Compounds of Sodium. Very interesting compounds are formed by the action of ammonia on metallic sodium. Sodium dissolves in liquid ammonia giving a blue solution, although, if the metal is present in sufficient quantity, a bronze-red tinge is observed by reflected light. A similar solution is obtained when sodium is treated with gaseous ammonia under pressure at low temperatures. If the pressure is afterwards reduced, so as to allow the excess of ammonia to escape, a crystalline solid,[2] with a red lustre surpassing that of copper, is left behind ; this has the composition $NaNH_3$. When preserved at ordinary temperatures, it tends to give off hydrogen, sodamide, $NaNH_2$, being left behind; but at low temperatures, such as –20° C., it decomposes in a different way, ammonia being evolved, and metallic sodium regenerated.

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[1] A. Schüller, *Zeitsch. Anorg. Chem.* **40** (1904), 385.

[2] A. Joannis, *Ann. Chim. Phys.* **7** (1906), 5.

Whilst at low temperatures, ammonia yields the additive compound just described, at higher temperatures ammonia reacts with sodium yielding sodamide and hydrogen. When sodium is heated in a current of dry ammonia at 300°–400°, a liquid is formed which, as long as free sodium remains, is blue; when all the sodium has been acted upon, the blue colour vanishes, and the liquid on cooling hardens to solid sodamide. Sodamide ($NaNH_2$) is colourless when pure, melts at 210° C., and volatilizes at 400°; the molten substance dissolves sodium metal, giving a blue solution. Sodamide reacts with water somewhat violently, yielding ammonia and sodium hydroxide.[1]

Analytical

The presence of small traces of sodium in a substance can be detected through the yellow colour which is imparted to a Bunsen flame. When the light from a flame containing sodium is examined by means of an ordinary spectroscope, a bright line in the yellow region (really a pair of lines very close together) is seen. Sodium produces no other lines in the visible portion of the spectrum. On account of its "monochromatic" character, the yellow sodium flame is invisible when viewed through cobalt blue glass.

Owing to the high solubility of the salts, there are few "precipitation tests" for sodium. However, when a solution of dihydroxytartaric acid, neutralized with ammonia, is added to a solution containing sodium, it yields a white crystalline precipitate of sodium dihydroxytartrate on stirring.[2] A crystalline precipitate is also formed on the addition of potassium antimoniate and a method of estimation depending on this fact has been worked out.[3] Generally speaking, however, it is best to effect the separation of sodium from other metals by the precipitation of the latter. The metals of all the groups, other than IA, can be precipitated either as insoluble sulphides, hydroxides, carbonates or phosphates. After this, potassium can be separated by hydroplatinic acid, in the presence of alcohol, as the sparingly soluble platinichloride. The filtrate contains the sodium, and the excess of hydroplatinic acid;

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[1] A method of obtaining sodamide in a state of purity is described in detail by L. Wöhler, *Zeitsch. Elektrochem.* **24** (1918), 261.

[2] H. J. H. Fenton, *Trans. Chem. Soc.* **67** (1895), 48.

[3] H. Weber, *Zeitsch. Anal. Chem.* **36** (1897), 513.

but the latter is easily decomposed if the filtrate is evaporated and the residue heated in hydrogen. After extraction of the residue with water, followed by filtration, platinum is left as a black, insoluble substance, whilst sodium remains in the filtrate.

When other metals have been removed, the sodium is converted to chloride or sulphate and weighed as one of these salts. Some care is needed, as both substances absorb moisture at a very appreciable rate from the air. The chloride is moreover distinctly volatile at a red heat; and precautions must be observed not to ignite it at too high a temperature. It is often preferable, therefore, to evaporate with sulphuric acid and weigh as the sulphate (Na_2SO_4). In this latter method, ignition at a rather high temperature is needed to eliminate all excess of sulphuric acid. The addition of ammonium carbonate to the crucible is sometimes recommended to aid the expulsion of the acid.

When sodium has been isolated as sodium chloride, it is possible, instead of drying and weighing the chloride, to determine the amount of chlorine present in the solution by titration with silver nitrate. From the result, it is easy to calculate the quantity of sodium.

TERRESTRIAL OCCURRENCE

Sodium is one of the most abundant elements that occur in the earth. The masses of molten silicate rock-magma which have, from time to time, been pushed up from the interior of the world into the crust, contain a considerable amount of sodium, which has tended to crystallize out as such complex silicates as

Albite, or soda-felspar .	$NaAlSi_3O_8$;
Other plagioclase felspars .	$xNaAlSi_3O_8 + yCaAl_2Si_2O_8$.

Soda-bearing minerals are not confined to one type of igneous rocks, but are found in granites, syenites, diorites and gabbros. Moreover, many other minerals occurring in all types of igneous rocks contain small quantities of sodium. One class of igneous rock, known as the *alkaline rocks*, which are peculiarly rich in alkali metals, are generally met with where an intrusion has come into contact with a basic country rock like limestone. It is probable, that interaction between the magma and the limestone has occurred at these points, and that the proportion of silica to bases has been reduced in the magma.[1] Thus, in cases where—but for the interaction of the limestone—the magma would have yielded, in the last stages of consolidation, a highly acid rock like granite or pegmatite (containing free quartz and highly siliceous minerals such as felspar), it actually yields a "nepheline-syenite" containing minerals poor in silica and rich in alkali, such as

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[1] R. A. Daly, "Igneous Rocks and their Origin" (McGraw-Hill); R. A. Daly, *J. Geol.* 26 (1918), 97; W. G. Foye, *Amer. J. Sci.* 40 (1915), 413; F. D. Adams and A. E. Barlow, *Canadian Geol. Surv., Mem.* 6 (1910), 227.

Nepheline $[Na,K]_8Al_8Si_9O_{34}$.

By the action of air and water on igneous rocks—an action which is aided by carbonic acid and organic acids derived from vegetation—sodium passes into the soil. All water which has passed through or over sodium-bearing rocks comes to contain sodium; thus sodium is a constituent of practically all river waters, and, in this way, is carried down into the sea. Unlike calcium and many of the other elements brought in solution into the sea, it is not utilized, to any extent, in the formation of the hard parts of marine creatures, but tends rather to accumulate, as sodium chloride, in the water. At the present time, ordinary sea-water contains, on the average, 2·7 per cent. of sodium chloride, out of a total 3·5 per cent. of dissolved solids; near the mouths of rivers the concentration is naturally less. Where, owing to earth-movements or other causes, a portion of the sea gets cut off from the rest, and rapid evaporation sets in so that the volume of the water steadily diminishes, the concentration of the sodium chloride increases very much. In this way, salt lakes, such as the Salt Lake of Utah or the Dead Sea in Palestine, are produced. The heavy waters of the latter contain about 9 per cent. of sodium chloride, the total solids amounting to 22 per cent. When the evaporation of such lakes has proceeded to a sufficient extent, the solution becomes supersaturated, and solid salt is deposited.[1]

Undoubtedly the important deposits of

Rock Salt $NaCl$

which occur in different parts of the world were formed by the evaporation of salt lakes in past geological ages. The salt-beds of Cheshire (England) and of Stassfurt (Germany) both occur in strata of the Triassic-Permian age, an age during which—as is known from independent evidence—dry, desert conditions existed over the northern part of Europe. Rock salt, formed no doubt in a similar way, occurs in all parts of the world. Important deposits are met with in the Carpathians, the Alps, in France, Spain, New York State, California, Kansas, Louisiana, and many other localities. The salt is naturally not pure sodium chloride, but contains also other soluble salts (such as calcium sulphate and magnesium chloride) which were present in the water before its evaporation; it is usually coloured yellow or reddish-brown owing to the presence of a little iron oxide.

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[1] The figures quoted in this paragraph are based on H. Ost's "Chemische Technologie" (Jänecke).

In a few cases, other sodium salts occur in large deposits, formed by the evaporation of lakes, usually situated in desert regions. In Egypt, and also in Wyoming (U.S.A.), the carbonate is found in the following forms:—

Natron . .	$Na_2CO_3.H_2O$
Trona . .	$Na_2CO_3.2NaHCO_3.3H_2O$

Both substances constitute a valuable natural source of alkali.

In the arid regions of Chili, vast quantities of the nitrate

Chili saltpeter . . .	$NaNO_3$

are met with. It is probably of organic origin, but many different explanations have been suggested to account for its existence in the present position. It seems likely that the mode of origin is as follows.[1] The large amount of water flowing from the Andes into the Pacific Ocean does not flow on the surface, but flows through underground courses below the Pampas. The soil is highly porous, and much evaporation occurs as it flows towards the sea. Now all waters in tropical lands contain nitrates, but the South American waters are particularly rich in them, probably owing to the presence of birds' deposits (guano). Hence the evaporation proceeding through the porous soil finally renders the water supersaturated with sodium nitrate, and the solid nitrate is left in the gravel a few feet below the surface, mixed with other sodium salts, notably the chloride, sulphate, and a trace of iodate. Another theory ascribes the ultimate origin of the nitrates to ammonium compounds given off in the vaporous state from the volcanoes of the Andes.[2] These become oxidized, it is thought, to nitrates.

Finally, certain lakes, notably the Borax Lake of California, contain, in addition to other sodium salts, sodium borate. The boron appears to have been derived from thermal springs. The incrustations of solid borax and other sodium compounds which are found in various parts of California and Nevada are evidently derived by the evaporation of such waters.

Various borates containing both sodium and calcium, such as

Ulexite . .	$NaCaB_5O_9.8H_2O$

occur in very large quantities both in California and also in South America (Chili, Peru and Bolivia). Crude borax also occurs in many other parts of the world, for instance in Thibet, from which country a considerable proportion of crude borax ("Tinkal") used to come. Of course, the commercial value of all such deposits rests upon the boron content rather than on the sodium.

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[1] J. T. Singewald and B. L. Miller, *Econ. Geol.* **11** (1916), 103.

[2] W. L. Whitehead, *Econ. Geol.* **15** (1920), 187.

TECHNOLOGY AND USES

Industries based upon Sodium Chloride

Rock-salt and sea-salt may be regarded as the prime sources of most sodium compounds.

The production of salt by the evaporation of sea-water is carried on in many countries. Around the Mediterranean, and notably near the mouth of the Rhone, as well as in Italy and Sicily, advantage is taken of the heat of the sun to evaporate the sea-water in shallow "pans." Such a process is only profitable in hot countries. It is interesting to note that the concentration of sea-water is also carried on in very cold regions, for instance the North of Russia, the water being separated as ice by freezing.

In the majority of countries, however, rock-salt is utilized. Where the salt occurs near the surface, it can be dug out by miners in the solid state. Where the layer of salt is far below the surface, a bore-hole is generally sunk to the necessary depth, and pumping machinery installed. Very often the well fills of its own accord with water, which, having found its way through the rock-salt bed, is saturated with the salt; in such a case it is only necessary to pump out the brine. If the well, however, does not keep full of liquid, it may be necessary to pump down water into the salt-bed periodically and after allowing time for it to become saturated, to pump it up again as brine.[1]

The evaporation of the brine[2] is carried out in many different ways, some of them being very primitive. Evaporation in open, shallow pans is still very common in Cheshire, the pans being of wrought iron, supported on brickwork, and heated directly by a fire below. The salt as it solidifies is drawn to the side with a perforated shovel or skimmer.

In many salt-boiling establishments, however, triple-effect evaporators have been installed, which allow of a considerable economy in fuel. In such evaporators, the brine is evaporated under reduced pressure; the boiling-point of any solution is of course lowered by reducing the pressure. The principle of a triple effect evaporator is shown in Fig. 2. There are three evaporating vessels, A, B and C, the pressure being highest in A and lowest in C. The liquid in A is raised to the boiling-point, by means of hot gases or steam passing through the heater H, and commences to evaporate. The steam thus produced in A passes out into the heater K of the next vessel B, and is still hot enough to keep the brine in B at the boiling-point corresponding to the lower pressure. The steam produced by the boiling of the liquid in B passes into the heater L of the vessel C, and causes evaporation of the brine here also; the pressure in this last evaporator is kept very low by means of an exhaust pump.

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[1] See G. Martin, "Industrial Chemistry" (Crosby Lockwood), Section XXII.

[2] A. F. Calvert, "Salt in Cheshire" (Spon). See also *Eng. Min. J.* 92 (1911), 633.

The salt which is precipitated in A, B and C as evaporation proceeds sinks to the bottom and collects in the salt-boxes S; periodically the salt-boxes are shut off from the evaporators, and the solid salt is discharged. Brine is run into the evaporators continuously to maintain the volume constant; the brine usually flows through the three vessels in turn, losing water by evaporation and salt by deposition in each "effect." In an evaporating plant of this kind the heat provided by the fuel is utilized to the fullest advantage.

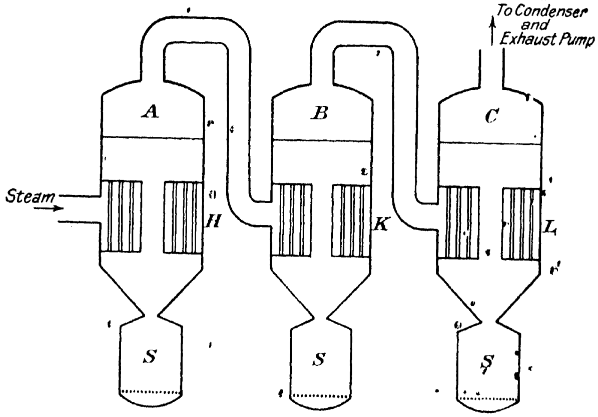

FIG. 2.—Triple Effect Evaporator.

The salt obtained by the direct evaporation of brine contains 1–2 per cent. of calcium sulphate, and a certain amount of magnesium chloride. This latter compound renders the salt unattractive for "table use," since the magnesium chloride absorbs moisture and causes the small grains to stick together, thus producing "lumps." In one form of "table salt" this difficulty is overcome by the addition of calcium phosphate (bone ash).

Where the brine is to be evaporated in a triple effect evaporator, it is preferable to carry out purification before the evaporation; otherwise crusts of calcium sulphate may be formed within the plant, causing obstruction. One method of purifying the brine is to treat it with lime, which precipitates magnesium as the hydroxide, and then with ammonium carbonate which throws down the calcium as insoluble calcium carbonate. Another method which is used in Cheshire is to electrolyse a small part of the brine, so as to produce sodium hydroxide. This is added to the main part of the brine, and the whole is treated with carbon dioxide gas; the calcium and magnesium are thus precipitated as carbonates.

Salt is used in considerable quantities in food preservation and in cookery, but a large proportion of the sodium chloride produced is consumed in the manufacture of other chemicals containing either sodium or chlorine.

Manufacture of Sodium Carbonate.[1] The most important process by which sodium carbonate and bicarbonate are now prepared from the chloride was first successfully worked by **Solvay** in France and Belgium. It has been greatly developed by Messrs. Brunner, Mond & Co., who successfully work the process in the Cheshire salt-fields.

It is essentially a precipitation process. When a concentrated solution of sodium chloride is treated with excess of ammonium bicarbonate, sodium bicarbonate, which is considerably less soluble than the other salts, is thrown down as a crystalline precipitate, whilst ammonium chloride remains in the solution

$$(NH_4)HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

In actual practice, instead of using ammonium bicarbonate as such, the brine is first saturated with ammonia, and then—after the removal of any impurities thrown down by ammonia—it is treated with carbon dioxide.[2] The fine bicarbonate crystals are then separated from the mother liquor, pressed and dried; if the normal carbonate (Na_2CO_3) is required, it is easily obtained by igniting the bicarbonate

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The ammonium chloride solution which forms the mother liquor must on no account be wasted. It is heated with lime, when ammonia gas distils off and is used to saturate more brine.

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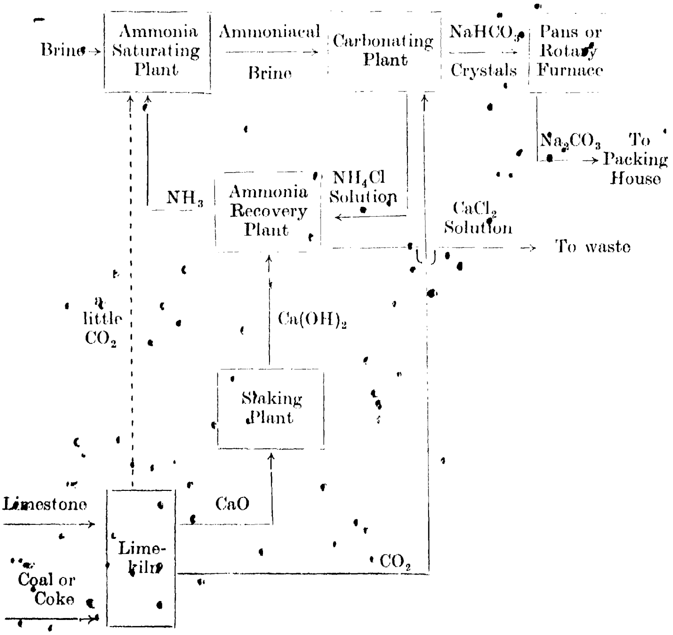
[1] G. Lunge, "Sulphuric Acid and Alkali" (Gurney and Jackson); G. Martin, "Industrial Chemistry" (Crosby Lockwood), Sect. 27 (by S. Smith); J. R. Partington, "The Alkali Industry (Ballière, Tindall and Cox).

[2] According to W. Mason, *Chem. Zeit.* 38 (1914), 513, sodium carbonate is first precipitated and converted at a later stage to bicarbonate.

$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O.$$

Thus the ammonia can be used over and over again, and upon this fact depends the success of the process. Of course, in practice, a small fraction of the compound escapes during each operation, but by the gradual perfection of the plant employed, the loss has been reduced to a minimum. In fact the difference between the successful and unsuccessful working of the process is largely dependent on the proper conservation of the ammonia, and, no doubt for this reason, very great secrecy regarding the details of the working methods is observed by manufacturers.

The lime required for the regeneration of the ammonia is obtained by burning limestone in kilns, and the carbon dioxide which is also generated in the lime-kilns is utilized for the precipitation of a further portion of sodium bicarbonate. Thus starting with sodium chloride and calcium carbonate (limestone) as raw materials, we end with sodium carbonate and calcium chloride, which is usually allowed to run to waste. The essential steps of the process are shown diagrammatically by a simplified "flow-sheet" below.



The principle of the process having been discussed, it is now possible to describe how it is put into practice. The sodium chloride required is generally pumped from the salt mine as concentrated brine; unfortunately, natural brine contains calcium and magnesium salts, which are injurious to the process, as these metals form carbonates far more insoluble than the bicarbonate of sodium. They must be separated from the solution, therefore, before the pure sodium compound can be precipitated. Consequently, when the brine is saturated with ammonia gas, a little carbon dioxide is introduced so as to form enough ammonium carbonate to precipitate the highly insoluble carbonates of calcium and magnesium, but not in such a concentration as would cause the separation of any sodium bicarbonate.

The treatment of the brine with ammonia gas (containing some carbon dioxide) takes place in a simple tank A (Fig. 3). The ammonia dissolves readily enough, but as the concentration increases there is a danger of some gas passing off, and so becoming lost. As this must be avoided, the gases leaving A are not allowed to escape directly into the atmosphere, but are passed up the absorbing-column B, down which a small portion of the brine passes on its way to the saturator A. The column B is so constructed that the brine flows from one floor (X) to another by means of the overflow pipes Y,Y, but each floor is always flooded with brine, up to the level of the top of these pipes; therefore the gases which pass up through the central openings Z,Z, must necessarily bubble through a layer of liquid on each floor. In this way very complete absorption of ammonia is brought about.

When the liquid in A is sufficiently saturated, it is pumped off through C, passed through a filter placed at D (not shown), to separate the precipitate of calcium and magnesium carbonates, and is then cooled by passing through a pipe-coil E immersed in cold water; this cooling is needed because the solution of ammonia, or indeed of any gas, results in a great evolution of heat. The clear ammonia-saturated brine is now ready for carbonation.

The saturation with carbon dioxide is a less simple operation than the saturation with ammonia. The carbon dioxide must be forced through it in very small bubbles; since otherwise the intimate contact needed for the complete solution of the gas will not be attained. The neutralization of carbon dioxide by ammonia causes a great evolution of heat, but if the temperature is allowed to rise too high, both carbon dioxide and ammonia gases will be lost by volatilization. On the other hand, it must not be too low, or the precipitate of sodium bicarbonate will be inconveniently fine, and the separation from the mother-liquor will be difficult.

The best temperature is about 30° C. One form of carbonator is shown at F; the carbon dioxide, obtained from the lime-kiln (and therefore necessarily diluted with nitrogen) is forced in under

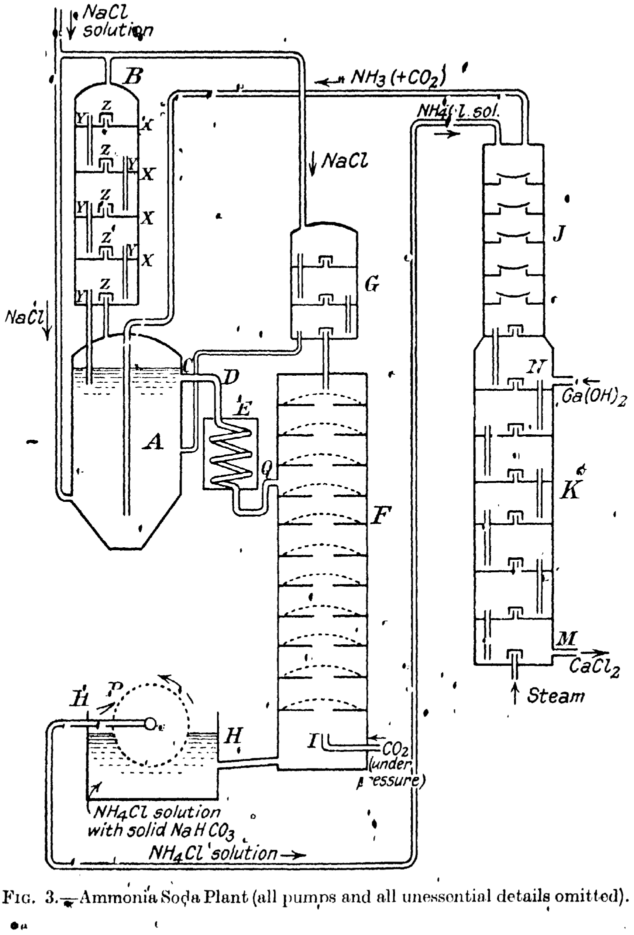


Fig. 3.—Ammonia Soda Plant (all pumps and all unessential details omitted).

considerable pressure at the bottom I of a tower filled with the ammoniacal brine, and rises up through numerous sieves of slightly lenticular form, which keep the gas broken up in minute bubbles and thus aid the complete absorption. The ammoniacal brine does not enter at the top of the column, since in that case much ammonia would be carried off by the gases. It enters the tower at Q, and as it descends through the tower becomes full of small crystals of sodium bicarbonate through the absorption of the carbon dioxide passing upwards. The cloudy liquid is drawn off from the bottom, and passes to a filter H.

In order to prevent the temperature in the carbonator from rising above 30°, numerous horizontal cooling pipes are fitted within the tower, and through the pipes cold water passes continuously. But since it is inevitable that the nitrogen of the lime-kiln gas will carry off a certain quantity of ammonia from the top of F, the gas is not allowed to pass directly away from the carbonator into the air, but is bubbled through another portion of brine in an absorbing column G similar to B; the small amount of brine used in this absorption flows into A.

The form of carbonating tower just described is the invention of Solvay. In spite of certain disadvantages it is believed still to be in use at most works using the Solvay process. It is, however, rather difficult to clean, and crusts of sodium bicarbonate—with traces of residual magnesium and calcium carbonates—are liable to form on the sieves and to block the holes. It has become usual to employ two carbonators in series. The liquid is partially saturated with carbon dioxide in one tower and the saturation is completed in the second. Since the precipitation only takes place in the second tower, the crusts are only formed in the latter. When the crusts have become sufficiently serious to obstruct the flow, the direction of the brine is altered so that it passes into the tower containing the crusts first, and into the clean tower afterwards. In this manner, the crusts are gradually dissolved away in the obstructed tower, whilst fresh crusts are produced in the tower previously clear. When these become serious, the course of the liquid is changed again.

The filter H, used to separate the solid sodium carbonate from the liquid, is usually of a continuous rotary type, consisting of a perforated drum covered with filter-cloth, half immersed in the liquid to be filtered. The drum rotates continuously and the interior is connected to a suction pump. The solid bicarbonate is retained on the outside of the filter cloth, and is scraped off by knives at P as the cylinder rotates, whilst the clear solution is sucked through the cloth and passes to the "ammonia recovery plant" JK.

This solution, as it enters the ammonia recovery plant, contains ammonium chloride and a little ammonium carbonate. Now the carbonate can be decomposed merely by passing steam through the solution; the steam will carry off ammonia and carbon dioxide.

But the ammonia occurring as chloride, requires to be liberated by the aid of lime (calcium hydroxide). The solution is therefore pumped up to the top of the tower JK and allowed to descend through it. Steam is passed up through the liquid from the bottom. The liberation of the ammonia present as carbonate is accomplished in the upper part (J) of the tower; milk of lime is then added at N, and consequently in the lower portions K the ammonia originally present as chloride is liberated also.

The ammonia gas (which contains a little carbon dioxide owing to the ammonium carbonate present in the liquor) passes back to the ammonia saturator A, and is used again to aid in the conversion of a further quantity of sodium chloride to bicarbonate. A certain small amount will be lost on each circuit, and a small quantity of ammonia (as ammonium sulphate) has to be added occasionally to the liquors in the tower JK to replenish that loss. The consumption of ammonium sulphate is, however,—with modern methods of working—only about 1 per cent. of the quantity of soda produced. The liquor running off from the bottom of K consists of a solution of calcium chloride containing a little unchanged sodium chloride.

The sodium bicarbonate is usually converted to normal carbonate by heating in a furnace, and the carbon dioxide then evolved is also often used at I. Since the ammonia is used over and over again, the raw materials of the complete process are really sodium chloride and calcium carbonate, and the final products sodium carbonate and calcium chloride. It is, therefore, in a sense correct to sum up the process *as a whole* thus,

$$CaCO_3 + 2NaCl = Na_2CO_3 + CaCl_2,$$

although this equation takes no account of the fact that much of the carbon dioxide used is ultimately produced by the combustion of the coal, which must of necessity be burnt in the lime-kiln. The by-product of the process is calcium chloride, for which there is very little demand. It will be observed that the whole of the chlorine present in the rock-salt used is to be found in the calcium chloride solution which emerges from M. This effluent is for the most part wasted; it is usually clarified by settling, to comply with the requirements of the law, and the clear liquor is then run into the nearest river.

Numerous attempts have been made to prevent the wastage of the chlorine contained in the rock-salt. This wastage does not occur in the old Leblanc process of making alkali—now practically obsolete—or in the newer electrolytic methods. It constitutes, therefore, the great drawback to the Solvay process. Nevertheless, in spite of a vast expenditure of time and labour to render successful a solution of the problem, none of the subsidiary processes by which it has been proposed to convert the calcium chloride into some useful product have come into general and permanent use.

Of the products of the ammonia-soda process, **sodium bicarbonate** ($NaHCO_3$) is itself used in the manufacture of "baking powder." The crude crystals produced upon the filter H contain too much ammonia for direct use. They are calcined to drive off these traces of ammonia, but, since carbon dioxide is partly driven off at the same time, the product must generally be recarbonated. The use of the bicarbonate in cooking depends upon the fact that it readily evolves carbon dioxide gas, and brings about the porosity of the doughy mass, which is thus caused to "rise"; most baking powders also contain acid substances, such as cream of tartar, which assist in the expulsion of the carbon dioxide. Cream of tartar is especially suitable since it is nearly insoluble in cold water, but dissolves when warmed; thus the gas is evolved gradually as the dough is heated. Sodium bicarbonate is also used in the manufacture of soda-water.

The **normal carbonate** (Na_2CO_3) is prepared by mildly igniting the bicarbonate in ovens, pans or rotary furnaces; the carbon dioxide which is given off is often used again in the carbonator. Alternatively the pasty mass of bicarbonate can be converted into the carbonate by treatment with steam, which carries off the carbon dioxide and any ammonia still present.

The direct product from the calcining furnace consists of the anhydrous *soda ash*, which represents a concentrated form for packing alkali, and is therefore favoured for export purposes; an even denser variety of sodium carbonate can be obtained by heating it more strongly. The decahydrate, $Na_2CO_3.10H_2O$ (*soda crystals*), can be obtained by crystallization from aqueous solution, and usually comes on to the market in large crystals. It is a very bulky form of alkali, but seems to be the most attractive form of soda in the eyes of small purchasers, who no doubt feel that they receive better value for their money when buying the voluminous decahydrate than when purchasing the dense soda ash. The monohydrate, $Na_2CO_3.H_2O$ (*crystal soda*), is produced by crystallizing the solution at a high temperature.

Whichever hydrate is chosen, the normal carbonate is employed very largely for the softening of water required for laundry work; the theory of softening is referred to in the section on "soap." Soda ash is also used largely in the glass-works, and a great deal of carbonate is used in soap-making, whilst a further quantity is converted into caustic soda. Sodium carbonate is, apart from lime, the cheapest alkali known, and is accordingly used in numerous cases—especially in organic chemistry—to neutralize acid solutions. It is used in the working up of the ores of many metals (such as tungsten) which possess oxides having acidic properties. Furthermore, it is used for the preparation of most other sodium salts.

Other Processes of obtaining Sodium Carbonate. A small amount of sodium carbonate is obtained by an **electrolytic** process closely related to the electrolytic method of obtaining sodium hydroxide; the consideration of this process can best be deferred, therefore, until the discussion of the manufacture of sodium hydroxide. (See page 37.)

Up to about the time of the war, a small amount of alkali was still made at a few works in England by the old **Leblanc process,** which fifty years ago supplied by far the greater part of the alkali of commerce. Since, however, it has now been almost completely displaced [1] by the far cheaper Solvay (ammonia-soda) process, it is only necessary to devote a few words to the older method. The chloride was first converted to sulphate by heating with sulphuric acid—according to the process still employed for the manufacture of sodium sulphate and hydrochloric acid. The sodium sulphate (" salt-cake ") was then strongly heated in a revolving furnace with limestone and coal; afterwards the black product (" black ash ") was extracted with water; the solution produced contained sodium carbonate, together with a certain amount of sodium hydroxide. The conversion is best explained by assuming that the coal first reduces the sodium sulphate to sulphide, and that—either during or previous to the extraction with water—double decomposition takes place, the insoluble calcium sulphide being produced,

$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

In the final years of the process, the sodium carbonate was not isolated in the solid state, the solution obtained being used for the preparation of caustic soda. The residue left after removal of the soluble alkali consisted principally of calcium sulphide. It was not wasted, but was worked up to produce either sulphur, or, alternatively, sodium thiosulphate (" Hypo ").

In addition to the alkali produced by the processes mentioned above, a certain amount of sodium carbonate is obtained from the natural deposits of alkali mentioned on page 22 and sometimes by evaporating the water of the soda-lakes themselves. The natural soda-industry is of considerable importance in the Western States of America, Egypt, and at Mogadi (East Africa).

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[1] See Report of Inspector Alkali Works, 1919. See also G. C. Clayton, *J. Soc. Chem. Ind.* **40** (1921), 443R.

Preparation of Sodium Hydroxide (Caustic Soda). Causticizing Process. Sodium hydroxide is to a very large extent made from the carbonate, by the action of lime. The change has already been explained in the theoretical section as being due to the fact that calcium carbonate is much less soluble than calcium hydroxide. But the reaction

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2NaOH$$

is never complete, and it is possible to calculate, from our knowledge of the solubilities of the two calcium compounds, how much sodium carbonate will be present in caustic soda solution obtained by stirring an excess of solid calcium hydroxide with a solution of sodium carbonate of known strength.

The process of causticizing can be described very shortly. A solution of sodium carbonate is boiled with " milk of lime " (calcium hydroxide mixed up with water), and separated from the excess lime and insoluble carbonate. The solution of caustic soda is then evaporated, multiple effect evaporators acting on the same principle as the triple effect evaporators mentioned in connection with brine, being employed ; often, however, there are six effects instead of three. The density of the solution gradually increases as water is driven off. Finally, when nearly all the water has been driven off, the fused sodium hydroxide that remains is allowed to run directly into sheet-iron drums. It solidifies in the drums as it cools, and, when full, the drums are sealed, to prevent the absorption of moisture by the alkali.

The main problem in connection with the causticizing process is that of separating the insoluble residue of lime and calcium carbonate from the solution. The separation was for a long time carried out by allowing the liquid to stand in a tank until the solids had settled, after which the clear solution was drawn off from above. This method, however, leaves the calcium compounds as a " mud," which, even when washed by decantation, is liable to retain an appreciable quantity of valuable alkali, and which, in any case, owing to its consistency, is very difficult to dispose of.[1] Filtration naturally suggests itself as a more efficient means of separating the solid from the solution, but great difficulties are encountered owing to the corrosive character of the hydroxide. The problem has, however, been solved by the use of mechanical filters, constructed of Monel metal, the employment of which produces the calcium carbonate residue in a comparatively dry form, which is actually capable of being used as a fertilizer for land which is deficient in lime.[1]

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[1] J. Hendrick, *J. Soc. Chem. Ind.* 33 (1914), 122.

Caustic soda made by the "causticizing process" is necessarily contaminated with sodium carbonate. The content of carbonate in the product is lowest, when a very dilute solution of carbonate is treated with lime. But, since the caustic soda has finally to be concentrated by evaporation, the alkali-maker, in the interests of economy of fuel, is unwilling to work with too dilute a solution, and consequently the purity of the product suffers. Another impurity occurring in the caustic is sodium chloride.

When the Leblanc process was employed to obtain the carbonate solution, sodium sulphide, sodium cyanide, and various iron compounds were generally present in the caustic manufactured. The product of the modern Solvay process is far less impure.

Electrolytic Manufacture of Caustic Soda.[2] **Diaphragm Processes.** A very large amount of sodium hydroxide is now made by electrolysis. When purified sodium chloride solution is electrolysed between insoluble electrodes, chlorine is produced at the anode,

$$2Cl' = Cl_2 + 2e,$$

whilst sodium hydroxide is produced in two steps at the cathode,

$$2Na^{\cdot} + 2e = 2Na$$

$$2Na + 2H_2O = 2NaOH + H_2.$$

We can summarize the reactions at both electrodes in a single equation :—

$$2Na^{\cdot} + 2Cl' + 2H_2O = Cl_2 + 2NaOH + H_2.$$

The anode must clearly be of some material unattacked by freshly liberated chlorine, and, practically speaking, the only cheap material which is suitable is carbon, although magnetite has also been used in Germany ; as a result of experience, manufacturers have succeeded in producing graphitized carbon in a form which can be used as an anode in chloride solution without undergoing undue disintegration. Almost any metal which is insoluble in alkali and which does not alloy with sodium, can be used as cathode, but it is advantageous to use iron or copper, owing to the low "hydrogen overpotential" of those metals.

So long as chlorine ions are the only anions existing in any large concentration at the anode, the production of chlorine and alkali proceeds according to the equations given above and the current efficiency is high. If, however, owing to the stirring up of the liquid, some of the alkali produced at the cathode finds its way to the anode, the discharge of $(OH)'$ ions, and the consequent evolution of oxygen instead of chlorine, may occur there. In other words, the current may commence to destroy alkali at the anode, whilst continuing to produce it at the cathode. It is, therefore, necessary to prevent the access of alkali to the anode surface.

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[1] M. L. Griffin, W. H. Howell and G. K. Spence, *Met. Chem. Eng.* **17** (1917), 599.

[2] See A. J. Allmand, "Applied Electrochemistry" (Arnold).

The obvious way to prevent alkali from passing from cathode to anode—as a result of the stirring up of the liquid by the gases evolved—is to interpose a porous diaphragm between the electrodes, thus dividing the cell into an anode compartment and a cathode compartment. So long as the hydroxide produced is confined to the cathode department, loss of efficiency can be avoided. At one time considerable difficulty was found in obtaining a material for the diaphragm, unaffected by caustic alkali and by chlorine, and yet sufficiently porous that the resistance of the cell was not unduly increased. Now, however, porous materials, consisting essentially of asbestos, can be produced which fulfil the requirements fairly well, although they tend to "clog" rather if the brine employed is not quite clear.

However, the division of the cell by means of a porous diaphragm does not permanently prevent the access of hydroxyl ions to the anode. For the passage of the current necessarily causes a movement of these ions from the cathode compartment through the diaphragm to the anode compartment. The only way to prevent this is to apply a slight hydrostatic pressure to the solution in the anode compartment so that the liquid as a whole moves in the direction

anode → cathode

at exactly the same rate as the ions would otherwise move in the direction

cathode → anode.

Thus by pressing the liquid through the diaphragm with the correct velocity, the boundary between chlorine and hydroxyl ions is kept somewhere within the partition, and the access of hydroxyl to the anode is avoided. An electrolytic cell, designed on such a principle, is continuous in its action; sodium chloride solution is continually forced into the anode compartment, and sodium hydroxide is continuously drawn off from the cathode compartment.

Numerous forms of cells have been designed, differing considerably in construction, but generally embodying the principles just set forth. As an example, the **Townsend cell**,[1] used at Niagara, may be described (Fig. 4). This is a long, narrow rectangular cell, the end-walls and bottom being of cement, and the sides of iron. There is a central anode compartment, containing the graphite anodes A; the anode compartment is separated from two cathode compartments on either side by diaphragms D of asbestos cloth; the cloth is rendered rather less permeable by being painted with a composition containing asbestos fibre, ferric oxide and gummy ferric hydroxide. The cathodes, C, consist of perforated iron plates, or grids, which are pressed into contact with the diaphragm and help to hold the cloth in place. The outer, or cathode, compartments are filled with a mineral oil. Purified sodium chloride solution is run into the anode compartment at a slight pressure, and usually stands a little higher than the oil outside, the level being carefully regulated. The slight difference in pressure on the two sides of the diaphragm causes the solution continuously to percolate outwards through the diaphragm. The sodium hydroxide solution, formed on the cathode grid, gathers there in droplets, which soon become detached from the cathodes owing to the evolution of hydrogen, and, passing into the body of the oil, sink to bottom and coalesce with one another; the solution of sodium hydroxide which collects is drawn off continuously through the pipes E, and passes to the evaporators.

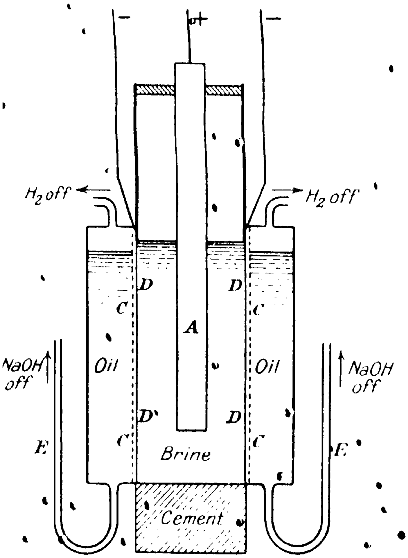

FIG. 4.—Principle of Townsend Cell.

Theoretically, only 2·3 volts are required to decompose sodium chloride so as to produce sodium hydroxide, chlorine and hydrogen. Actually, in order to carry out the decomposition at a reasonable rate, about 4 volts are applied to each cell. Normally a row of cells (perhaps 30 to 60) are connected in series, and the appropriate E.M.F. (e.g. 120 volts if there are 30 cells, allowing 4 volts per cell) is applied between the ends of the row. Usually the cell-house contains several of these rows of cells arranged side by side. Thus, although the individual cells are small (the original size of the Townsend cell was 8 × 3 × 1 ft.) the combined output of the house is considerable. The current efficiency is about 96 per cent.

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[1] L. H. Baekeland, *J. Soc. Chem. Ind.* **26** (1907), 746; *Electrochem. Ind.* **5** (1907), 209; **7** (1909), 313; C. P. Townsend, *Electrochem. Ind.* **1** (1902), 23; H. K. Richardson and R. L. Patterson, *Trans. Amer. Electrochem. Soc.* **17** (1910), 311; A. B. Hooker, *Met. Chem. Eng.* **23** (1920), 961.

From each cell, hydrogen escapes from the cathode compartment through the tubes to hydrogen mains which collect the gas from all the cells. Similarly the chlorine formed at the anode passes through tubes to chlorine mains. The hydrogen is in some works wasted, but in others is used for "hardening" oils. The chlorine is a most valuable product. It can be liquefied, and compressed into cylinders, or used in the manufacture of bleaching powder; alternatively it is employed in the production of various organic substances containing chlorine. The liquid chlorine and bleaching powder are mainly used for bleaching, sterilization and disinfection; but, during the war, there was great demand for chlorine as a poison gas, and the manufacturers, in many cases, came to regard chlorine, rather than alkali, as their main product.

Many other types of cells are used at different works.[1] The device of filling the cathode compartment with oil is peculiar to the Townsend cell. In some cells, the cathode compartment is kept full of alkali solution, which is drawn off at the same rate as brine is added to the anode compartment. More often the cathode compartment is empty of liquid, the alkali being allowed to drip from the cathode grid into a trough below.

If steam and carbon dioxide is passed into the anode compartment, sodium carbonate can be produced instead of hydroxide. A certain amount of carbonate is manufactured in this manner in Cheshire. The electrolytic manufacture of carbonate presents, in one respect, less difficulty than that of the hydroxide, because, the mobility of the CO_3'' ion being but small, there is little fear of the brine in the anode compartment becoming seriously alkaline.

The shapes of different cells used in the manufacture of caustic soda vary very much. The large **Nelson** cells[2] installed during the war in America have the diaphragm and the perforated cathode in the form of a **U**-shaped trough, supported in a rectangular tank.

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[1] A summary of the forms still in use is given by E. Chaleyer, *Rev. Prod. Chim.* **22** (1919), 613.

[2] C. F. Carrier, *Trans. Amer. Electrochem. Soc.* **35** (1919), 239.

In England, on the other hand, a round cell with porous partition of cylindrical shape has been used recently. In Germany, there has been a tendency to develop types of cells with horizontal diaphragms. One variety of the **Billiter** cell,[1] much used in the Rhineland and elsewhere, is a rectangular tank containing, just above the bottom, a nearly horizontal cathode of iron gauze, upon which the diaphragm (formed of an asbestos—barium sulphate composition) is spread. Above this comes the anode compartment filled with brine, in which the graphite rods forming the anodes dip. Brine is run in at the top, and caustic soda drawn off from below the diaphragm. The hydrogen produced at the cathode runs along under the diaphragm, which is slightly sloped so as to facilitate the escape of the gas, and passes off at an outlet at the side.

In all the cells mentioned above, in which the brine is run into the anode compartment and passes through the diaphragm to the cathode compartment, the penetration of sodium hydroxide to the anode is avoided. But this arrangement does not necessarily prevent a certain amount of chlorine reaching the cathode, for chlorine is fairly soluble in water and a considerable quantity travels to the cathode in aqueous solution. Should free chlorine enter the cathode compartment it may react with the alkali to produce hypochlorites or chlorates, or it may combine with the sodium as it is formed, and thus reduce the current efficiency. When the solutions employed are warm (which is, in any case, desirable, so as to reduce the resistance of the cell), the solubility of chlorine in the brine is only slight, and the loss of efficiency is not serious. Nevertheless, it is worth considering whether the loss could not be avoided altogether, and for this reason a cell designed by **Finlay**[2] deserves mention, although it has not, apparently, found wide application.

The cell contains two vertical diaphragms arranged between the two vertical electrodes, and thus dividing the cell into three compartments. The brine is run into the middle compartment, and passes outwards through both diaphragms into the anode and cathode compartments. Sodium hydroxide solution is drawn off from the cathode compartment, while a certain amount of brine, saturated with chlorine, runs off continuously from the anode compartment. It can be boiled free from the gas, and used again. The current efficiency of this cell is naturally unusually high, and is said to reach 98 per cent. But the second diaphragm adds to the resistance of the cell and it does not necessarily follow that the consumption of energy is less in the Finlay cell than in others.

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[1] A. J. Allmand and E. R. Williams, *J. Soc. Chem. Ind.* **38** (1919), 285**R**; A. J. Allmand, *Trans. Faraday Soc.* 9 (1913), 3.

[2] F. G. Donnan, J. T. Barker and B. P. Hill, *Trans. Faraday Soc.* **5** (1909), 49.

Mercury Cells. An entirely different method of obtaining sodium hydroxide from salt, which dispenses with the use of a diaphragm, depends on the employment of mercury as a cathode material. If sodium chloride is electrolysed between a carbon (or platinum) anode and a mercury cathode, little or no hydrogen is evolved, but a fairly stable sodium amalgam is formed. This is, no doubt, due to the high overpotential of mercury. If, however, the amalgam, when formed, is run off into another compartment, and treated with water, whilst in contact with a substance of low "hydrogen overpotential," such as iron or carbon, the short-circuited cell or couple

Sodium Amalgam	Water	Iron or Carbon

is set up. The amalgam is thus decomposed, sodium hydroxide being produced in solution, whilst hydrogen is evolved on the iron or carbon.

A generalized diagram of a mercury cell is shown in Fig. 5.

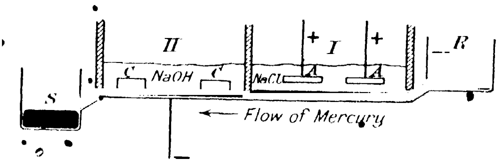

FIG. 5.—Generalized Form of Mercury Cell.

Brine is electrolysed in the main chamber I; the anodes A,A are of carbon, graphite or platinum, whilst the cathode is formed by thin stream of mercury running across the floor of the chambe from the reservoir R. The mercury, as it passes out of the cel contains sodium in solution, and runs into the decomposer I where it comes into contact with the contact-pieces C of graphit or iron, and at the same time with water. The sodium amalgar is quickly decomposed, yielding sodium hydroxide, and nearly pur mercury passes out into S and can be pumped back once more t the reservoir R.

As soon as the concentration of sodium in the amalgam become at all high, the sodium is likely to be attacked by the chlorin dissolved in the brine, regenerating sodium chloride. Therefor in order to obtain a high current efficiency, it is important t keep the concentration of sodium low by circulating the mercur quickly through the system. The various forms of mercury cell used by different makers differ essentially in the means of causing the mercury to pass between one chamber and the other. The Castner-Kellner Alkali Company, to whom the development of the mercury cell is largely due, are believed now to utilize an Archimedean screw to raise the mercury from the level of S to that of the reservoir R.[1] In their original form of cell mercury was caused to flow to and fro between the two compartments by rocking the entire cell; this arrangement was inefficient and would be extravagant of power except when applied to small units; it has been abandoned. In the **Whiting cell**,[2] which has found employment in America, a rotary pump is fitted to raise the mercury to the necessary level. The action of this cell is intermittent; every two minutes valves open, and allow the amalgam to flow from the main cell to the decomposer, its place being taken by fresh mercury from the reservoir. An Austrian firm[3] employs compressed air to force the mercury from one compartment to the other, and then back, whilst in one German process, the circulation of mercury is effected by means of an ingenious arrangement of "paddles."[4]

Since the amount of water admitted to decompose the amalgam can be limited, it is possible to prepare comparatively concentrated sodium hydroxide solution. In this respect, the mercury processes have a certain apparent advantage over the diaphragm processes, which can never yield an alkaline solution more concentrated than the brine employed. It is, however, scarcely correct to regard the saving of fuel in the evaporators as representing a true economy, because the production of the comparatively strong alkali usually involves a higher expenditure of electrical energy. As a matter of fact mercury cells usually require an E.M.F. of nearly 5 volts per cell, whilst diaphragm cells often work with less than 4 volts per cell. On the other hand, mercury cells, unlike diaphragm cells, yield an alkali quite free from chlorides.

Comparative Commercial Merits of Processes. The current efficiency of electrolytic alkali production with modern cells is high, always over 90 per cent.; but, since the E.M.F. required for the normal working of each cell usually greatly exceeds the theoretical value of 2·3 volts, the energy efficiency varies between 45 per cent. and 65 per cent. It is the energy efficiency which determines the amount of alkali which can be made from each K.W.H. of electrical energy, and, where—as in England and

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[1] R. Tassig, *Trans. Faraday Soc.* **5** (1910), 258.

[2] J. Whiting, *Trans. Amer. Electrochem. Soc.* **17** (1910), 327.

[3] *Chem. Zeit.*, Rep. **37** (1913), 412.

[4] M. Wilderman, *Eighth Int. Cong. App. Chem.* (1912), Vol. **21**, 185.

Germany—the electrical energy has to be generated by means of coal, the success or failure of the process will depend upon this point. So long as there is a demand for chlorine and for hydrogen, the electrolytic production of caustic alkali is likely to compete successfully with the alternative method of causticizing sodium carbonate obtained by the Solvay process, even where coal is the ultimate source of power. In America, and countries where water-power is comparatively plentiful and electric power therefore cheap, the electrolytic process has a considerable advantage.

Uses of Caustic Soda. Caustic soda is used very largely in the paper and textile industries, and also in the manufacture of soap as described below. It is also employed in the preparation of many organic bodies, notably the dye-stuff alizarin. Furthermore, it is source of sodium metal, which is in turn the source of sodium peroxide and of sodium cyanide.

Manufacture of Sodium Hypochlorite. It will be convenient at this point to discuss the preparation of sodium hypochlorite, a substance used very largely both for bleaching and for the sterilization of drinking-water. As in the case of sodium hydroxide, there are two methods of preparation, the first being a precipitation process depending on the insolubility of calcium carbonate, and the second consisting in the electrolysis of sodium chloride, under conditions rather different from those required for the preparation of sodium hydroxide.

In the first process, chlorine is passed over slaked lime, yielding bleaching powder, according to the method to be described in the section on calcium. The milky solution of bleaching powder, which can be regarded as containing calcium hypochlorite and calcium chloride, is then treated with sodium carbonate; insoluble calcium carbonate is precipitated, whilst sodium hypochlorite, mixed with sodium chloride, is left in solution. This process is probably the most economical where the substance has to be prepared on a large scale. The hypochlorite is but rarely isolated in the solid state, but is sold as a solution; the solution decomposes quickly unless it is protected from the action of light and carbon dioxide. It is most stable if kept slightly alkaline, but its oxidizing activity is most pronounced in the presence of acid.[1]

On account of the rather poor keeping qualities of sodium hypochlorite, many manufacturers, who require comparatively small quantities of sodium hypochlorite for bleaching purposes, prefer to make it themselves, rather than purchase it from the large scale producer; in such cases, the electrolytic process is of service. It was stated above that, in the manufacture of sodium hydroxide by electrolysis, the chlorine and sodium hydroxide produced at the two electrodes must be kept apart; if the manufacture of hypochlorite is aimed at, they are allowed to mingle. Hypochlorite is formed by their interaction, thus:—

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[1] See E. K. Rideal and U. R. Evans, *J. Soc. Chem. Ind.* **40** (1921), 64R.

$$2NaOH + Cl_2 = NaClO + NaCl + H_2O.$$

The temperature must be kept low, for in a warm solution the hypochlorite decomposes, giving rise to chlorate,

$$3NaClO = NaClO_3 + 2NaCl.$$

But even at low temperatures, hypochlorite will be converted to chlorate by electrolytic oxidation at the anode. Hypochlorite is also destroyed, if it is allowed to come into contact with the cathode, being reduced once more to chloride, from which it was formed. It follows, therefore, that after a certain amount of hypochlorite has been formed in the salt solution, a "stationary state" will be reached, at which the concentration of hypochlorite ceases to increase further, the salt being destroyed as quickly as it is formed.[1] It is useless to continue the electrolysis further; the complete conversion of chloride to hypochlorite by electrolysis is practically impossible.

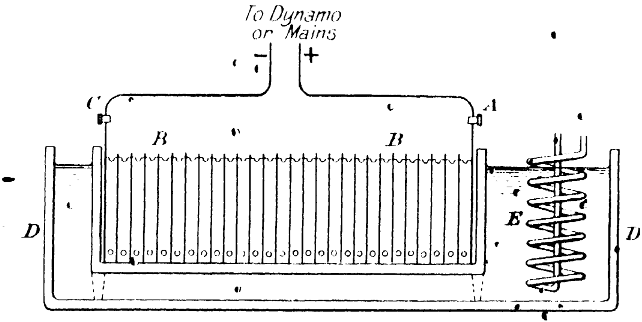

FIG. 6.—Electrolyser for the Preparation of Sodium Hypochlorite.

Many different forms of "electrolyser" have been designed for the purpose of converting a solution of sodium chloride into hypochlorite.[2] One of the types designed by Haas and Oettel (Fig. 6) may be described as an example.[3] A rectangular trough B of earthenware is fitted with a series of twenty-nine vertical graphite electrodes, which divide the trough into a series of twenty-eight narrower compartments. The two end electrodes, A and C, are connected to a dynamo yielding about 115 volts; each of the intermediate electrodes functions as a cathode on one side, and an anode on the other. Thus the plant is really a set of twenty-eight cells in series. The trough stands in a larger tank containing sodium chloride solution, and the liquid circulates through the inner trough during the passage of the current, entering it at openings in the base and overflowing at the top into the outer tank. This continuous circulation is brought about by the evolution of hydrogen gas at the electrodes, which carries the liquid upwards. The outer tank contains cooling pipes, E, through which cold water passes continuously, and thus the liquid entering the inner trough is always cool; it overflows before the temperature has risen to an extent which would cause serious loss of efficiency; in practice the temperature should be kept below 24° C.

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[1] P. H. Prausnitz, *Zeitsch. Elektrochem.* **18** (1912), 1025.

[2] For the different patterns see A. J. Allmand's "Applied Electrochemistry" (Arnold).

[3] F. Oettel, *Zeitsch. Elektrochem.* **7** (1901), 319.

In many of the pre-war models of electrolyser, platinum electrodes were employed, but the present scarcity of the metal renders it necessary to look for a cheaper material; carbon electrodes are nearly equally efficient, but tend to disintegrate somewhat.

In the making of hypochlorites no attempt is made to divide the cell into anodic and cathodic compartments by porous diaphragms of the kind used in alkali-making, so as to restrict the contact of the hypochlorite with the electrodes. It is possible, however, to add to the solution small quantities of substances which produce a film over the surface of the electrodes; this film, whilst not interfering with the passage of current, prevents unnecessary access of the hypochlorite to the active electrode surface, and thus minimizes the destruction of the unstable salt. A very common addition is potassium chromate; it is said to form a film of an insoluble chromium oxide on the cathode.[1] "Turkey-red oil," and various other complex organic substances, form, in the presence of lime, a film upon the anode; a combination of chromate and "Turkey-red oil" has been recommended, so as to produce a film on each electrode. But a very simple addition, which forms a good film on a carbon cathode, is lime alone; the adhesion and permanence of the layer is greatly increased if a colloid, such as wheat-starch, is also present. Lime is said to be practically useless with a platinum cathode.[2]

If the electrolyser is constructed of Portland cement, it is stated that films appear spontaneously on both electrodes, without any additions. No doubt, the cathode films consist of the basic oxides present in the cement, whilst those on the anode may consist of silica.

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[1] E. Müller, *Zeitsch. Elektrochem.* **5** (1898–99), 469; **7** (1901), 398; **8** (1902), 909.

[2] E. Müller and M. Buchner, *Zeitsch. Elektrochem.* **16** (1910), 93

However produced, the presence of the films on the electrodes notably raises the current efficiency of the process, and allow a higher concentration of hypochlorite in the solution to be reached.

Besides its use as a bleacher, sodium hypochlorite is largely used in "textile finishing" as it prevents the growth of certain algæ which give rise to stains.[1] It is used in very many places for the sterilization of the public water-supply. The employment of hypochlorites for this purpose developed mainly in America, but it has since been adopted at many places in this country. Part of the water-supply of London is now treated with sodium hypochlorite. It is likewise added in many places to the water of swimming-baths. During the war, specially prepared hypochlorite proved a most useful antiseptic for the treatment of wounds.

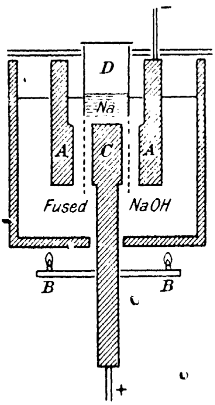

Fig. 7.—Cell for Preparation of Metallic Sodium.

Manufacture of Metallic Sodium. Sodium is almost invariably produced by the electrolysis of the hydroxide in the fused state. The products of electrolysis are oxygen at the anode, and sodium at the cathode. The sodium being lighter than the fused caustic soda, floats up to the surface in the molten condition, and the main precaution to be observed is to prevent it from being burnt either by the air or by the anodically produced oxygen. The temperature must not be too high, or the sodium will expel hydrogen from the hydroxide, producing the anhydrous oxide (Na_2O).

A form of cell which has been used successfully in England, the United States and Germany, is shown diagrammatically in Fig. 7. The cathode C, consisting of an iron rod, is surrounded by a ring anode A of nickel-iron alloy; as a rule, a cylinder of wire gauze is interposed between them. The caustic soda of the bath may in the first instance be fused by gas-burners B, but, when once molten, the heat generated by the current should be sufficient to keep the bath molten; the temperature ought not to rise much above the melting-point of caustic soda, or the current efficiency will suffer. About 4·5 to 5 volts is applied to the cell. The sodium formed on the cathode rises to the surface, together with any hydrogen produced, and is caught in the closed cylinder D placed just above. Since D is full of hydrogen the sodium is not oxidized, and may be ladled out periodically. The oxygen from the anode escapes without destroying the sodium. The nickel-iron anodes are not seriously attacked in the fused solution, for they become "passive"—probably a protective layer of closely adherent oxide is formed upon them. As the sodium hydroxide is decomposed, fresh caustic soda is added, and thus the process can be made continuous.

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[1] F. D. Toyne, *J. Soc. Chem. Ind.* **31** (1912), 477.

Very many attempts have been made to obtain sodium by the direct electrolysis of the fused chloride, since this naturally occurring compound is much cheaper than the hydroxide, which is, of course, itself prepared from the chloride. Great difficulties, however, are met with, which have not yet been overcome. In the first place, sodium chloride fuses at a much higher temperature than the hydroxide (803° instead of 327°), and there is more difficulty in keeping it in a state of complete fusion. At this high temperature, moreover, all the substances concerned, sodium chloride, chlorine and sodium, are extremely corrosive, and the containing vessels are likely to be quickly destroyed. Furthermore, sodium is extremely volatile at these ranges (it boils at 877°), and, what is more serious still, the metal is, to all intents and purposes, soluble in molten sodium chloride; probably it is not soluble in the strict sense of the word, but forms a "metallic fog" consisting of minute metallic particles of colloidal size distributed through the salt. Even in the electrolysis of the fused hydroxide, the sodium tends to form a fog to some extent, and minute globules of the metal find their way to the anode and are destroyed. Owing, no doubt, to the lower temperature, the phenomenon is not—in the case of sodium hydroxide—fatal to the process, although it lowers the current efficiency considerably. But, in a fused chloride, the fog formation is so serious as to render the process almost unworkable.

Metallic sodium is used mainly for the preparation of the cyanide and of the peroxide; it is employed, to some extent, in organic chemistry, both as a reducing agent and a dehydrating agent.

Cyanide. Commercial "cyanide" may consist of sodium cyanide, potassium cyanide, or a mixture of the two. It plays a most important part in the metallurgy of gold and silver, and is also employed in the electro-deposition of both metals.

A good deal of cyanide is prepared from the potassium ferrocyanide obtained at gas-works, as a bye-product in the purification of coal-gas. The modern method is to heat the potassium ferrocyanide with metallic sodium, whereby a mixture of cyanides is obtained

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The quantity of cyanide obtainable by that process is, however, quite insufficient to meet the demand, and many other methods of manufacture have been introduced. Of these, **Castner's process,** used on a large scale at Frankfurt, also involves the use of metallic sodium.[1] Dry ammonia gas is led over molten sodium giving sodamide, and the sodamide is then fused with coal or charcoal yielding cyanide. The reaction can be expressed,

$$NaNH_2 + C = NaCN + H_2,$$

but is generally believed to take place in two stages, sodium cyanamide (Na_2N_2C) being the intermediate compound.

$$2NaNH_2 + C = Na_2N_2C + 4H$$
$$Na_2N_2C + C = 2NaCN$$

Beilby's process, employed at Glasgow, does not require the employment of metallic sodium. Potassium carbonate (mixed with a little cyanide from a previous operation, so as to lower the melting-point) is fused, and treated with charcoal in small quantities, ammonia gas being forced through the molten mass

$$K_2CO_3 + 4C + 2NH_3 = 2KCN + 3CO + 3H_2.$$

If care is taken not to add the charcoal in too large quantities, the product is white, and sufficiently pure. Earlier (German) attempts to prepare cyanide by this reaction led to a black product, which had to be leached and recrystallized before it was fit for the market.

During the war, another important method of making cyanide was developed in America, namely by heating calcium cyanamide with sodium chloride in an electric furnace.[2] A little calcium carbide is added to the charge to prevent "foaming."

Very many other methods of obtaining cyanides have also been suggested, and some have been used on a large scale.

Sodium peroxide is made by passing dry air, free from carbon dioxide, over metallic sodium, at 300°. The sodium is cut into slices and placed on aluminium trays which are exposed to the current of air in iron tubes, the passage of air being arranged on the "counter-current principle"; the fresh air passes first over the tray containing material almost completely converted to peroxide, and only when the air has lost most of the oxygen does it come in contact with fresh sodium.

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[1] B. Waser, *Chem. Zeit.* **37** (1913), 1521.

[2] W. S. Landis, *Trans. Amer. Electrochem. Soc.* **37** (1920), 653.

Sodium peroxide is largely used in bleaching. In many cases, and especially where wool has to be treated, the alkalinity of the solution is first reduced by the addition of sulphuric acid, or of magnesium sulphate.

Manufacture of Hydrochloric Acid and Sodium Sulphate ("Salt-cake"). Another manufacturing process of which sodium chloride forms the starting-point, although less important at the present time than was formerly the case, is the preparation of hydrochloric acid and sodium sulphate; they are produced by the action of sulphuric acid on salt. The operation is now carried out mainly for the sake of the hydrochloric acid, but, in the days of the Leblanc alkali-process, it constituted the first step in the manufacture of sodium carbonate and sodium hydroxide. The decomposition occurs in two stages. The first, which leads to the formation of bisulphate,

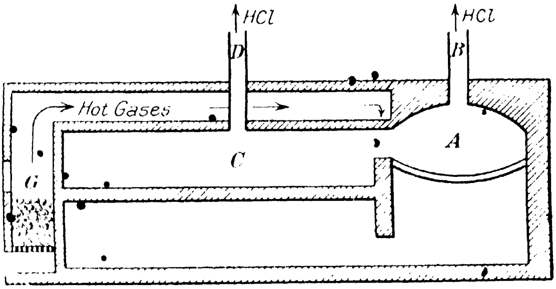

FIG. 8.—Simple Salt-Cake Muffle Furnace.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

takes place at a comparatively low temperature, whilst, in the second stage, which requires a much higher temperature, the bisulphate liberates a further quantity of hydrogen chloride :-

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The type of furnace which is still largely used for the operation is shown in Fig. 8. The salt and sulphuric acid are placed in the pan A, which is warmed merely to a moderate temperature. Here the first stage of the reaction occurs, the hydrogen chloride escaping through the pipe B. The mass of bisulphate and salt is then raked into the muffle C, which is heated red hot by flames from the grate G; the flames pass first above the muffle and then below it, finally passing under the pan and helping to raise the temperature there also. In the muffle, the second stage of the reaction takes place, the hydrogen chloride passing away through the pipe D.

During the second stage of the process the charge must be stirred up with rabbles. In the form of furnace just described, this is done by hand, although it is heavy work. Many attempts have been made to introduce mechanical furnaces into the salt-cake process, and of these Mactear's furnace, which dates from 1879, is still much used.[1] In this furnace (Fig. 9), the bed of the hearth is essentially a circular saucer, set on wheels W, which run on a circular rail-track, R, below. Mechanism is provided which causes the hearth to rotate continuously about a vertical axis. The mixture of salt and acid is fed continuously into the depression D at the centre of the bed and is gradually mixed and pushed towards the edge by stirrers S,S,S (both fixed and rotating), with which it comes in contact as the bed rotates. The whole is heated by hot gases from a grate which pass through flues F,F above and below the rotating hearth (or in the older type of furnace play directly on the charge). By the time the charge reaches the circumference of the rotating bed, and is pushed off into the annular trough T, the conversion into salt cake is complete. The chief disadvantage of the Mactear furnace, and indeed of all mechanical rabbling devices, is that corrosive gases (in this case hydrogen chloride) invariably attack the mechanism.

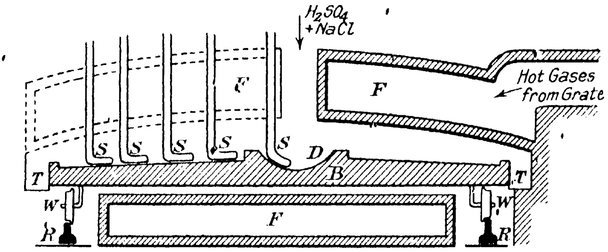

FIG. 9.—Mactear Furnace.

Whatever type of furnace is used, the hydrogen chloride produced passes off through pipes, which are usually carried through the air for some distance, so as to cool the gases. The gases then travel through a condensing plant where the hydrogen chloride is condensed in water, yielding hydrochloric acid. Often the condensation of the first portion is brought about by the passage of the gases through a series of earthenware pots containing water. But in general the absorption of the last portions of the hydrogen chloride is effected in some form of condensing tower, down which water is allowed to pass ; the hydrogen chloride is removed by the water, hydrochloric acid being collected at the bottom. It is important to let no appreciable quantity of hydrogen chloride escape into the air, as the acid fumes are extremely destructive, especially to vegetable life. In most countries, there are now very strict regulations regarding the amount of hydrogen chloride allowable in the "exit gases." Escape of the gas may occur not only through inefficient condensation by the water, but also by leakage. This is particularly likely to occur at the muffle, which is liable to become cracked owing to the high temperature. The furnaces are, therefore, usually so controlled that the pressure in the flues is slightly in excess of that in the muffle. If, therefore, a slight crack in the walls should establish communication between the muffle and the flues, the leakage will be inwards, and not outwards ; the hydrogen chloride will be contaminated with flue gas, not the flue gas with hydrogen chloride.

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[1] See *J. Soc. Chem. Ind.* 4 (1885), 534. Various other types of mechanical furnaces are described by G. Lunge, "Sulphuric Acid and Alkali" (Vol. II) (Gurney and Jackson).

In the **Hargreaves process,** sulphur dioxide, air and steam are used in the place of sulphuric acid, the separate manufacture of the acid thus being rendered unnecessary. Porous blocks of salt, formed by pressing together powdery salt whilst damp, are treated with the gaseous mixture at a temperature of 500° C. The reaction is extremely slow, and not only the temperature, but also the proportion of steam and air, require careful regulation. At the end of a few weeks, the cake of salt has been completely converted to sodium sulphate.

It is found that the reaction is accelerated somewhat if the oxide of iron or copper is present as a catalyst ; it has therefore become customary to introduce salts of iron or copper into the damp sodium chloride before it is pressed into blocks.

Sodium sulphate is commonly known as "**salt-cake,**" on account of the tendency of the salt to cake together to a hard mass. It is used, to some considerable extent, in glass-making ; it is also the source of sodium sulphide, whilst the hydrate (Glauber's salt) has a limited use in medicine.

Sodium sulphide is made by heating sodium sulphate with coal, or coke, in a revolving furnace.

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

After the reaction is over, the furnace is discharged, and the black mass extracted with water ; the solution is separated from the excess of fuel, and then evaporated until the amount of water remaining is less than that corresponding to the solid hydrate $Na_2S.9H_2O$. The liquid is then allowed to run into casks or drums, in which it solidifies. It is employed considerably in the preparation of "sulphur dyes," and also in tanneries for removing hairs from the hides.

Borax or sodium borate ($Na_2B_4O_7.10H_2O$) is another sodium compound made on a very large scale; the commonest method depends on the decomposition of naturally occurring calcium borates with a boiling solution containing sodium carbonate and bicarbonate. After removal of the precipitated calcium carbonate by filtration, the hot solution is run into tanks, in which the borax crystallizes out in glittering crystals. The anhydrous salt (borax glass) is obtained on igniting the hydrate; it is used as a constituent of many glasses, enamels and glazes, and finds employment in metallurgy as a flux.

The **chlorate** and **perchlorate** of sodium are used to some extent for the same purposes as the corresponding potassium salts, and are prepared by methods analogous to those which will be described in the section on potassium. They are naturally cheaper than the potassium salts, but, being more soluble, are less easy to prepare in a pure state; moreover, being more liable to absorb moisture, they are less suitable for many purposes, such as match-making, although quite useful for the manufacture of aniline black and similar substances.

Fatty Salts of Alkali-metals. Soaps

Soaps consist essentially of the sodium or potassium salts of various fatty acids, or mixtures of such salts. They are manufactured, as a rule, by the action of caustic soda upon fats, which can be regarded as the glycerine salts of the fatty acids in question.

Glycerine is an organic hydroxide, $C_3H_5(OH)_3$, which interacts with acids such as

Palmitic acid . . .	$C_{15}H_{31}.COOH$
Stearic acid . . .	$C_{17}H_{35}.COOH$

to form salts.

Glyceryl palmitate .	$C_3H_5(COO.C_{15}H_{31})_3$
Glyceryl stearate . .	$C_3H_5(COO.C_{17}H_{35})_3$

These salts are often referred to as the "glycerides" of palmitic and stearic acids respectively.

The fat of the hog, sheep and ox contain both the glycerides just mentioned, together with an "unsaturated" glyceride derived from oleic acid, an acid containing less hydrogen than stearic acid,

Glyceryl oleate .. $C_3H_5(COO.C_{17}H_{33})_3$

The supply of animal fats available for soap-making is, however, comparatively small, and it is necessary to rely largely upon vegetable oils, such as cocoa-nut, palm-kernel, and cotton-seed oils, as raw materials in soap-boiling. In addition, various oils derived from fish have been brought into use. All these substances, which are liquid at ordinary temperatures, contain a large proportion of "unsaturated glycerides," and in general yield a soap of somewhat softer consistency than that given by saturated glycerides.

When a glyceryl salt of a fatty acid is heated with caustic soda solution, "saponification" takes place.[1] The sodium hydroxide displaces the glycerine and the sodium salt of the acid in question is formed. Thus caustic soda boiled with glyceryl stearate produces sodium stearate and glycerine. From the aqueous solution of soap, made by boiling fats with caustic soda, the solid soaps can be obtained by the addition of sodium chloride (salt) to the liquid. The concentration of sodium ions is so much increased by this addition that the limit of solubility of the sodium soaps is exceeded. In consequence, the soap separates out almost entirely from the solution.[2] The glycerine was at one time allowed to separate with the soap, and this is still the practice in the preparation of some "toilet soaps"; but, in general, glycerine is now considered too valuable a compound to be wasted, and is recovered from the solution after the soap has been separated.

The process of soap-boiling is not complicated. The fat, previously melted, and the caustic alkali solution are run into a large tank or "soap-kettle," which contains coils through which steam is passed in order to heat the mixture to boiling-point. Steam is sometimes driven directly into the liquid to promote the mixing. When the saponification is complete, salt is added, which causes a separation of the soap from the aqueous solution; the soap, which is liquid and lighter than the solution, rises to the top, and the watery liquid, which contains excess of caustic soda, along with the sodium chloride and most of the glycerine, can be drawn out from below. Usually, however, the saponification is still incomplete, the soap containing some undecomposed fat. It is customary, therefore, to boil it with a further quantity of caustic soda, until this fat also is saponified. The soap is then boiled with water, and is finally run molten into frames where it solidifies; afterwards it is cut into bars or cakes by machinery.

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[1] For theory of saponification see M. H. Norris and J. W. McBain, *Trans. Chem. Soc.* **121** (1922), 1362.

[2] For theory of salting out see J. W. McBain and A. J. Burnett, *ibid.* 1320.

Yellow soaps contain a certain amount of "rosin," a substance which is cheaper than most fats. It is not to be regarded entirely as a diluent or adulterant because it is itself capable, to some extent, of saponification. Many soaps contain sodium silicate as a "filler." Toilet soaps are especially carefully prepared, so as to be as free as possible from uncombined alkali; any hydroxide that may remain is usually converted to carbonate by treatment with carbon dioxide. Sometimes, unsaponified oil is incorporated with the soap, which fulfils a similar function in reducing the alkalinity.

The glycerine of the alkaline liquors from soap-making is in general recovered, but a certain amount is always lost. During the war, glycerine acquired a very considerable importance for the manufacture of explosives, and the methods of soap-making were regulated so as to enable the maximum quantity of glycerine to be recovered. One general method is to break up the fat into the free fatty acid and glycerine by suitable treatment, and afterwards to neutralize the fatty acid with alkali, so as to obtain soap; this procedure also enables the maker to employ sodium carbonate in the place of the more expensive hydroxide as the source of alkali.

Various methods have been used at different times to break up the fats into fatty acids and glycerine. Superheated steam alone—if introduced under considerable pressure and a temperature of about 160–180° C.—is capable of effecting the hydrolysis. It is preferable, however, to use an acid as a catalyst, since it is then possible to work without excessive pressures, and yet to carry out the hydrolysis more quickly than with steam alone. In the **Twitchell process,** which is largely used, the fat is boiled with dilute sulpho-benzene-stearic acid (or some similar acid) for a few hours. Afterwards the product is allowed to separate into two layers, the fatty acid above, and a watery layer containing glycerine below. The boiling must be conducted in a vessel from which air is excluded; otherwise dark-coloured products are formed. There is no doubt that the true catalytic agent in the Twitchell process is the hydrogen ion. All acids are capable of causing the hydrolysis of organic bodies of this character. The special virtue of the complex organic acids employed in the Twitchell process is that, by the use of such reagents, the mutual solubility of the oily and watery phases is increased.[1]

The "splitting" of the fat can be also brought about by means of certain organic catalysts known as "enzymes." Many fats decompose into glycerine and the fatty acid spontaneously in the presence of these enzymes. Butter, for instance, is well known to become "rancid" if kept too long, because—owing to the presence of an enzyme—one of the fatty constituents (glyceryl butyrate) hydrolyses into glycerine and butyric acid, the latter substance possessing the well-known unpleasant taste and smell. An analogous spontaneous hydrolysis of fats in the presence of a suitable enzyme ("lipase") has been employed on a considerable scale for soap-making in Germany.

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[1] E. Briner and A. Trampler, *Helv. Chim. Acta*, **5** (1922), 18.

In the Krebitz process of soap-making[1] which is worked at Chicago, calcium hydroxide is used to decompose the fat. This yields the sparingly soluble calcium soap, which, after washing to remove all the glycerine, is decomposed with sodium carbonate; insoluble calcium carbonate is precipitated, and sodium soaps remain in solution, and may be "salted out" by the addition of sodium chloride. The advantage of the process is that practically all the glycerine is recovered.

"**Soap powders**" usually contain, besides soap, anhydrous sodium carbonate (soda ash). One of its functions seems to be to absorb any moisture that may find access to the mixture, and thus to prevent the particles of soap from sticking together; it also, no doubt, serves to soften the water.

Theory of Detergent Action of Soap. The reason why soap possesses a unique value as a cleansing agent has long been a subject of speculation. It has for many years been known that it possessed some power of loosening the film of fat or grease which allows "dirt" to cling to a surface. Formerly the grease-solvent power of soap was ascribed to the alkaline reaction of the solution; it was pointed out that other alkaline solutions, such as those of ammonia or borax, also possessed a power of removing certain fats. This explanation, however, is clearly wrong; the fat-solvent properties of strong ammonia, for instance, is due to the fact that it attacks the fats forming an ammonium soap. The alkalinity of soap solutions is, however, due to the break up (or hydrolysis) of the soap itself through dilution with water; and it is almost inconceivable that the alkali thus formed should—at the same dilution—be able to decompose further fat, forming fresh soap, and thus reversing the hydrolysis reaction. Moreover, soap removes many substances, such as mineral oils, which are unattacked by alkalis.

The fat-removing power of soap is now known to be due to its emulsifying properties. When soap solution and an oil are rubbed together, the fat becomes subdivided into minute particles which remain suspended in the soap solution. The relative ease of formation and the stability displayed by emulsions formed in soap solutions—as compared with those obtained by shaking oil with ordinary water—is to be explained by the abnormally low interfacial tension between soap solution and the oil[1]; it is thought that one important factor is the formation, upon the surface of the oil globules, of a protective skin, which prevents them from coalescing. In addition it appears that a soap solution exerts a true solvent action upon certain substances (e.g. paraffin) which are quite insoluble in water.[2]

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[1] G. A. Wrisley, *J. Ind. Eng. Chem.* 8 (1916), 732.

The colloidal character of concentrated soap solutions has already been discussed in Chapter VII.

Softening of Water. The fatty salts of calcium and magnesium are insoluble. This is very unfortunate, since most waters contain soluble salts of these metals. Consequently when soap is dissolved in ordinary water its fatty acids are at once precipitated as calcium and magnesium salts, and no "lather" can be obtained until sufficient soap has been dissolved to react with the whole of the calcium and magnesium present. Consequently, before water is suitable for laundry work, it must be "softened."

The soluble salts of calcium and magnesium which are found in water are the bicarbonates and sulphates. The bicarbonates are decomposed by boiling, carbon dioxide being evolved and the insoluble normal carbonates being precipitated. Thus the hardness due to bicarbonates is called "*temporary hardness*" and can be removed by boiling the water. Another way of dispelling temporary hardness is to add the proper quantity of milk of lime to the water; the hydroxide reacts with the bicarbonate yielding the normal carbonate again. In some towns where the water is so hard as to be injurious even for drinking purposes the whole of the public supply is softened with lime in this way. The "*permanent hardness*," due to the presence of the sulphates, is not dispelled by boiling or by the addition of lime. It is removed by adding sodium carbonate to the waters, which precipitates the calcium and magnesium present as insoluble carbonates.

A certain amount of water is now softened by the so-called "**Permutit**" process; the water is allowed to pass through vessels containing a layer of solid "zeolites," or hydrated silicates of sodium and aluminium. Double decomposition occurs.[3] Calcium takes the place of the sodium in the zeolite, and the water, after the treatment, contains harmless sodium salts in the place of harmful calcium salts. When the zeolite has absorbed a large quantity of calcium, and is consequently becoming less effective, it is possible to re-actify it by treatment with a concentrated solution of sodium chloride; the reverse action occurs, calcium being replaced by sodium. The zeolite can then be used as a water-softener for a considerable further period.

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[1] S. A. Shorter and S. Ellingworth, *Proc. Roy. Soc.* **92** [A] (1916), 231; R. T. A. Mees, *Chem. Weekblad*, **19** (1922), 82; E. E. Walker, *Trans. Chem. Soc.* **119** (1921), 1521.

[2] S. U. Pickering, *Trans. Chem. Soc.* **111** (1917), 86.

[3] For theoretical details of the change see A. G. Schulze, *Zeitsch. Phys. Chem.* **89** (1914), 168; *Zeitsch. Elektrochem.* **26** (1920), 472; V. Rothmund and G. Kornfeld, *Zeitsch. Anorg. Chem.* **103** (1918), 129.

In spite of the success of this and similar softening processes, the discovery of some cheap fatty acid, having a soluble calcium and magnesium salt, would be extremely welcome. The sodium salt of such an acid would constitute a soap which could be used effectively with hard water without any previous treatment and without the employment of sodium carbonate.

Industries based upon Sodium Nitrate

Although sodium nitrate is not used, to any great extent, as a source of sodium compounds, the chapter would be incomplete if some reference was not made to the important industry which depends on Chili saltpetre as raw material. The caliche, or crude nitrate, contains, as it is mined in Chili, a great deal of insoluble material, stones, sand and clay, as well as sodium chloride, various sulphates and a trace of sodium iodate. It is subjected to a rough refining in Chili.[1] The caliche is extracted with boiling water in tanks fitted with false bottoms, and the solution is drawn off from the coarser insoluble constituents; it passes through settling tanks, where much of the lighter impurities, which have been carried off in suspension, settle to the bottom. It is often found, however, that many of the particles, being of colloidal size, do not settle, and the problem of separating the lighter clay particles is not yet entirely solved, although the installation of continuous filtration plants is said to have given fairly satisfactory results.

The liquid finally passes into crystallizing tanks where the nitrate crystallizes out; the product obtained still contains some chloride, but most of the iodate—which is of importance as being the principal source of the world's supply of iodine—remains in the mother liquor.

The nitrate thus obtained is shipped to countries where it is required; a considerable quantity coming to England. It is, of course, mainly employed as a *nitrogenous fertilizer*. Nitrate is probably the most suitable form of nitrogen for unlimed soils; for calcareous soils, the salts of ammonia are thought to give better results.[1] In wet weather sodium nitrate possesses the disadvantage of being washed away by the rain more quickly than ammonia salts. Sodium nitrate is a more rapid fertilizer than ammonium sulphate, because—under ordinary conditions—the ammonia has to be oxidized to nitric acid, by means of bacteria existing in the soil, before it can readily be assimilated by the plant. It may be mentioned here that calcium cyanamide, another nitrogenous fertilizer, is slower still in action; it probably passes through two stages before becoming active, first being converted to ammonia, which in turn gives rise to nitric acid.

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[1] I. B. Hobsbaum and J. L. Grigioni, *J. Soc. Chem. Ind.* **36** (1917), 52. See also F. G. Donnan, "Report on Programme of Investigation for the Chilian Nitrate Industry" (1921) (Chilian Nitrate Committee).

A considerable amount of Chili saltpetre is used for the manufacture of **nitric acid**; for this purpose it should be as free as possible from chlorides. The nitric acid is produced by heating Chili saltpetre with sulphuric acid. As in the case of the manufacture of hydrochloric acid, two stages are possible:—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$
$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3$$

But the second stage requires a very high temperature for completion, and, in any case, produces a substance (Na_2SO_4) which has an inconveniently high melting-point. In the practical manufacture of nitric acid, therefore, the main bye-product is the bisulphate ($NaHSO_4$) mixed with its anhydride ($Na_2S_2O_7$).

The operation is carried out in iron retorts heated in a furnace; the nitric acid distils off and condenses in pots, the last portions being absorbed in a tower. The mixture containing bisulphate is taken out of the retorts in the molten condition, and when solidified is known as "nitre cake." It has an acid reaction, and is used where a cheap acid liquor is required. During the war, when sulphuric acid was scarce, it was used, in the place of that acid, in the manufacture of hydrochloric acid and also in the manufacture of ammonium sulphate. Nitre cake has also been employed in the treatment of water. In spite of various suggestions,[2] the problem of how to utilize the bye-product has not fully been solved.

Nitric acid is, of course, largely used in the manufacture of high explosives and of the intermediary substances required in the preparation of dyes. A great deal is now prepared from atmospheric nitrogen, either through direct combination of the nitrogen and oxygen of the air effected by means of the electric arc, or by the oxidation of ammonia, which may itself be produced from atmospheric nitrogen. In spite of the success abroad of the last-mentioned method of fixing atmospheric nitrogen, the manufacture of nitric acid from Chili saltpetre is likely to continue in this country for many years to come.

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[1] J. G. Lipman and A. W. Blair, *Soil Sci.* **9** (1920), 371; C. E. Thorne, *Soil Sci.* **9** (1920), 487.

[2] J. Grossmann, *J. Soc. Chem. Ind.* **35** (1916), 155; **36** (1917), 1035; W. H. H. Norris, *J. Soc. Chem. Ind.* **40** (1921), 208T.

Glass [1]

General. A brief reference was made to the condition of matter known as the "glassy state" in the introduction. It will be necessary to recall here the main points of our conceptions of that state. When a fused salt is cooled down below a certain temperature (the freezing-point), crystallization commences at certain places within the mass, and extends outwards from these points until the whole is solid; the process of crystallization apparently consists in the atoms arranging themselves in orderly array according to some definite and specially stable arrangement. If, however, the fused salt be already viscous at the temperature in question, the process of crystallization occupies a considerable time; and, if the salt be cooled down quickly through the freezing-point to a low temperature, at which the viscosity becomes very high, crystallization may be avoided altogether. We thus arrive at a "glass," a mass in which the atoms and molecules exist in "disorderly" fashion, as in a liquid, but which possesses a rigidity comparable to that of a crystalline substance. At fairly high temperatures at which glass is "soft," it is correct to regard glass as an extremely viscous liquid; but it is probable that at low temperatures the molecules lose almost completely their "translatory" motion, and link up with one another in a network of chains of more or less permanent character, thus accounting for the rigidity of the material.[2] A glassy solid differs from a crystalline solid only in the fact that the atoms or molecules are not arranged according to a definite plan, on a space lattice. The structure of a glass is comparable to that of a "gel." Probably "solidified" glass bears the same sort of relation to "fused" glass as a "gel" does to a "sol."

We may expect to obtain the glassy state most easily in compounds which are viscous just above their melting-points. The silicates, the borates, and the phosphates are compounds of this character. It has already been stated that anhydrous borax cooled down fairly quickly hardens to a clear glass, and the same is true of many silicates and phosphates.[1] Now, if instead of taking one single silicate, we take a mixture of two or three silicates, we naturally depress the crystallizing-point to a temperature at which the viscosity of the melt is infinitely greater than at the crystallizing-point of a single substance, and in such cases it may be possible to cool the mixture exceedingly slowly and yet to obtain a glass. In fact, if the composition of the silicate melt be chosen rightly, it should be possible to keep the glass produced at a comparatively elevated temperature for hours together without any perceptible crystallization (or devitrification) occurring. Glass which is to be of practical utility must, in general, be capable of being " annealed " without appreciable devitrification,[2] although it seems possible that even in the best glasses minute crystals may commence to form if the annealing is continued long enough.[3] In inferior glasses, devitrification occurs more easily, silica being the substance deposited in most cases. Certain glasses which devitrify spontaneously are, however, purposely made for use where a semi-opaque substance is desired; many of the " milk-glasses " are of this character.

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[1] W. Rosenhain, "Glass Manufacture" (Constable).

[2] M. W. Travers, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 62. Compare C. V. Raman, *Nature*, **109** (1922), 138.

A glass has, of course, no definite melting-point, but it is convenient to speak of the " softening-point " of a glass, by which is meant the temperature at which the glass begins to " flow " perceptibly under the influence of a small force, such as that of gravity. It is probably not an exact physical constant. Indeed, glass can be said to flow slowly at ordinary temperatures; for if a long piece of soft glass tubing is allowed to lean against a wall for some time, it is found to lose its original straightness.

Unlike a crystal, a glass has no cleavage planes, or directions of especial weakness; it is probably upon this fact that the mechanical strength of glass—as contrasted with an aggregate of crystalline silicates—depends.

Glassy substances are frequently met with in nature and in industry. The silicate rock-magma which, when cooled slowly deep in the earth's crust, yields the crystalline rock granite, produces the glassy lava rhyolite when cooled quickly on the earth's surface. Many of the silicate mixtures (" slags ") which pour forth from furnaces during metallurgical operations cool to masses of glassy character.

Commercial glass is essentially a mixture of silicates in proportions chosen to render the glassy state stable under the conditions to which the material is to be subjected. The silicates present are normally those of sodium (or potassium) and calcium, but the presence of lead, aluminium, magnesium, barium, and zinc may be desirable in order to give the glass the refractive index, softening-point or coefficient of expansion suitable to the uses to which a particular glass is to be put. Iron is often present as an important constituent, since it occurs in most of the cheaper raw materials employed. In addition, it may be convenient—in order to obtain the required properties—to have borates or phosphates present in the mixture. Certain substances, manganese dioxide, sodium nitrate, arsenious oxide or selenium, may be added to prevent discoloration of the glass by undesirable impurities (such as iron or sulphur), or to mask the colour where it cannot be prevented. In other cases, where a coloured glass is desired, small amounts of colouring substances may be added, whilst, if a semi-opaque glass is to be prepared, the mixture may contain an opacifier. These points will be considered in further detail at a later stage.

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[1] Compare E. Kittl, *Zeitsch. Anorg. Chem.* **77** (1912), 335.

[2] N. L. Bowen, *J. Amer. Ceram. Soc.* **2** (1919), 261.

[3] Sir H. Jackson, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 61.

Raw Materials. Glass is always made by melting together a carefully proportioned mixture of the necessary constituents at a high temperature. The glass mixture or " batch " usually contains *silica* in the form of sand ; for most glasses (and especially for optical glasses) an extremely pure quartz sand, with low iron content, is desired. Before the war, most of the glass sand used in this country was imported from Holland, Belgium, and France, but it is known that there are many British sands—notably at Aylesbury —of suitable quality.[1] *Sodium* or *potassium* may be added as carbonates. Unless the glass is to contain lead, however, the sodium is more often added in the form of the sulphate, which is cheaper. Where the sulphate is employed, coke is also added to the charge, and, on melting, the sulphate is reduced to sulphite, and the volatile sulphur dioxide is then expelled by the silica, sodium silicate being formed. Potassium is sometimes added as nitrate. *Aluminium* may be added as hydroxide, or as kaolin (hydrated silicate) ; but in common glasses it is often added as granite or basalt, iron being thus introduced in considerable quantities into the batch ; in some finished glasses found to contain aluminium, it is clear that much of this aluminium was not added intentionally, but has been derived from the fireclay of the pots or tanks. *Calcium* may be introduced either as carbonate or oxide, *barium* usually as carbonate, *magnesium* and *zinc* generally as oxides. *Lead* is almost always added as red lead ; as there is a danger of lead being reduced to the metallic state, it is not unusual to include potassium nitrate, as an oxidizer, in a glass batch containing lead. *Borates* are introduced as boric acid or borax. If required, one of the decolorizers mentioned above is added. Usually the batch contains a large quantity of *cullet* or broken glass from a previous operation, which acts as a flux for the less fusible constituents. It is generally necessary for the materials of the batch to be finely ground.

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[1] P. G. H. Boswell, " A Supplementary Memoir on British Resources of Sands and Rocks used in Glass Manufacture " (Longmans).

Melting of the Glass Mixture. In the older glass works, the batch was melted down in fireclay pots, and pot furnaces are still used where comparatively small quantities of high quality glass are needed, e.g., for optical purposes. Where large quantities of ordinary glass are required, it is now usually melted in large tanks lined with fireclay, set in a gas-fired furnace, arranged so that the flames of burning producer gas play over the surface of the glass in the tanks. A "*regenerative*" glass furnace is shown diagrammatically in Fig. 10; the glass batch is contained in the tank T, whilst the producer gas and air enter respectively through the chambers D and C containing brick chequer-work, which has previously been heated. They thus enter the furnace proper distinctly hot, and, on mixing, burn, causing a temperature of 1,400° C. above the glass; the burnt gases pass out through the chequer-work chambers A and B. After a time, when the brick-work in A and B has become very hot, and that in C and D has become cooled to a corresponding extent, the direction of the gas is altered by means of valves V_1 and V_2, and the gas and air are

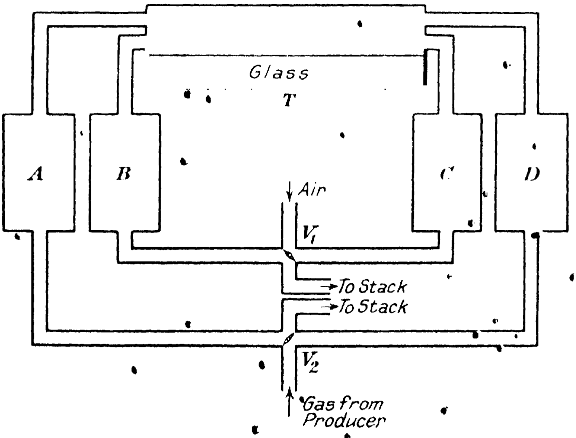

FIG. 10.—The Regenerative System of Heat Economy.

allowed to flow in through the hot chambers A and B, whilst they flow out through C and D. This "regenerative" system effects a great saving of fuel.

An alternative system of fuel economy, known as the "*recuperative*" system, is coming into use. The principle is shown in Fig. 11. The gas and air before entering the furnace pass through tubes, and the hot waste gases leaving the furnace pass out through the space surrounding these tubes, thus preheating the gas and air which are entering. The periodic operation of valves is not, in the recuperative system of heat economy, needed.[1]

The character of the refractory materials used for lining a glass furnace is most important. There is no difficulty in finding substances which remain unfused at the temperature in question (which is distinctly lower than that of a steel furnace), but there is a danger that the lining may actually interact with the molten silicates. If the refractory were decidedly acid, or decidedly basic, interaction would occur. Fire-clay, however, being a comparatively neutral material, can be used with satisfactory results for the tanks or pots, and for parts of the furnace with which the glass is likely to come in contact; silica bricks must, for structural reasons, be employed for the crown of the furnace. Refractory materials differ very much

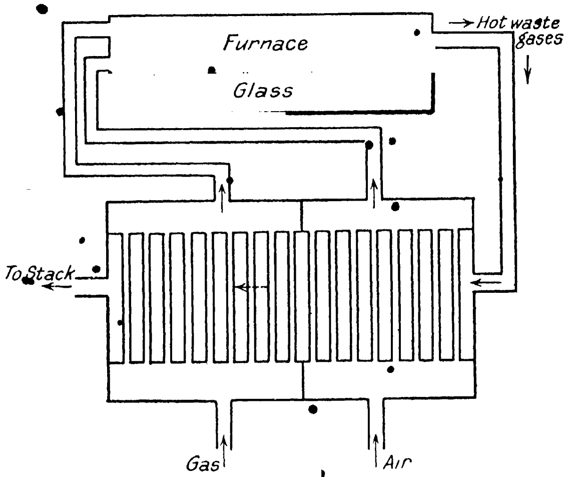

Fig. 11.—The Recuperative System of Heat Economy.

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[1] W. G. Fernsides, *Trans. Soc. Glass Tech.* **1** (1917), 109; W. Rosenhain, *Trans. Soc. Glass Tech.* **1** (1917), 130.

from one another in the way they are attacked by the glass. Some become evenly worn away, others are attacked locally and become pitted; as in the corrosion of metals, it is this last type of attack which is especially serious.

The mixture must be thoroughly melted, a process occupying 10–12 hours. If sufficient time is not allowed, the pieces of unmelted material remain as "batch stones" in the finished glass; "stones" may, however, be produced in other ways, for instance, through fragments of the pot or tank lining becoming loosened by erosion, or through the falling in of pieces of the brickwork covering the furnace.[1]

The first portion of the melting usually involves frothing due to evolution of carbon dioxide or sulphur dioxide. After this has subsided the glass is usually stirred with fire-clay stirrers so as to obtain absolute uniformity. Samples are taken out at intervals and examined for clarity and workable properties. Considerable difficulty is often experienced owing to the retention of bubbles in the glass, and it is generally necessary to raise the temperature during the latter stages of the process, in order to render the glass more fluid and thus hasten the rising of bubbles. Where the bubbles existing in the mixture are small, they rise particularly slowly, and various devices are used to free the glass from small bubbles. One method, mentioned by Rosenhain, consists in introducing a potato, by means of an iron fork, into the glass. The rapid upward rush of large bubbles from the potato carries to the surface the small bubbles previously existing in the glass. When the batch is absolutely clear and uniform in composition, the glass is ready for use.

It lies outside the province of this book to describe the means by which the glass comes to assume the various shapes with which we are familiar. It may, however, be mentioned that **bottles** are produced on an enormous scale by means of a machine in which small portions of hot glass are blown by air pressure into the interior of a mould of appropriate shape. Wide-mouthed bottles, and also glass tumblers, are made in a rather different machine, the glass being pressed into the mould by means of a plunger, although here also the shaping is completed by air pressure.

Window glass is obtained by blowing a huge pear-shaped bubble of glass, one end of which is cut off, the mouths being widened until it assumes the form of a cylinder open at both ends; the cylinder is slit lengthwise with tongs, and flattened out by rolling on a hot fire-clay slab. On the other hand, **plate glass**, used for large windows, mirrors and glass shelves, is made by pouring glass on to a flat table and rolling flat; after annealing, it is ground to the required thickness and polished. Continuous methods of producing glass in sheets are coming into use.[1] In one American process, a continuous sheet of glass is drawn from a pool of molten glass in a compartment of the melting-furnace, and passing in a plastic condition over a roller, is carried forward horizontally through the annealing "lehr"; the rate of travel is about 2 to 6 feet per minute, according to the thickness of the sheet which is being made.

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[1] J. Bowen, *J. Amer. Ceram. Soc.* 1 (1918), 594.

Annealing. Whatever shape the glass may have been forced to assume, it will always—if cooled quickly—be in a state of internal stress. The glass will generally be in a state of compression on the surface, which must have cooled and stiffened whilst the interior was still hot and soft, and in tension in the inner portions. These stresses have been shown to exist in quickly cooled glass by an optical method.[2] The internal stress by itself may be insufficient to produce an effect on the material, but the smallest blow may cause a slight additional stress which will bring up the total stress above the "maximum strength" of the glass, and fracture will occur. Thus the glass in this state is brittle. It is necessary, therefore, to anneal glass for some hours, that is to heat it a little below the softening temperature for some considerable time, and then allow it to cool slowly. At the annealing temperature, the molecules possess sufficient translatory motion to prevent the retention of internal stresses, and the glass obtained after the slow cooling is free from undue fragility.

Quickly cooled glass, however, although in a state of strain, is often extremely hard. By pressing glass whilst in the plastic state between metal plates, the surface of the slabs produced becomes so hard that it can scarcely be scratched with a diamond. This variety of glass is used in the preparation of "cellar-lights." The cause of the special hardness of pressed glass requires further investigation.

Composition of Different Glasses.[3] The proportion of the different ingredients is chosen according to the purpose for which the glass is required. Window glass often has a final composition, approximating to the following:—

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[1] E. W. Tillotson, *J. Soc. Chem. Ind.* 40 (1921), 155T. Compare W. E. S. Turner, *J. Soc. Chem. Ind.* 39 (1920), 431R.

[2] See also R. L. Frink, *Eighth Int. Cong. App. Chem.* (1912), Vol. V, 97.

[3] The percentage compositions given are only approximate, and are set forth simply to show the sort of proportions in which the different oxides occur. Much information regarding the composition of glass is given by A. B. Searle in Sect. 73 of G. Martin's "Industrial Chemistry" (Crosby Lockwood). But the theoretical views expressed in that work, founded on Asch's theory, must be accepted with caution.

$$SiO_2\ 73\%,\ Na_2O\ 13\%,\ CaO\ 12\%,\ Al_2O_3\ 2\%.$$

Bohemian glass, which is used for hollow ware, contains potassium as the main alkali-metal, and may have the composition,

$$SiO_2\ 72\%,\ Na_2O\ 3\%,\ K_2O\ 13\%,\ CaO\ 11\%,\ Al_2O_3 + Fe_2O_3\ 1\%.$$

Some authorities consider that equally good glass could be made with sodium as the only alkali-metal, the employment of potassium being—according to this view—merely a matter of custom.

Common bottle glass often contains much iron on account of the cheap materials used, and also manganese as a decolorizer; for instance,

$$SiO_2\ 64\%,\ Na_2O\ 10\%,\ CaO\ 14\%,\ MgO\ 4\%,\ Al_2O_3\ 2\%,\ Fe_2O_3\ 3\%,\ MnO\ 3\%.$$

For chemical apparatus, glass is often required which is especially resistant to reagents. In general, glass especially rich in silica will be resistant to acids, whilst that rich in alumina will be resistant to alkalis.[1]

In other cases, one may require a glass of especially low softening-point (e.g. for soft glass tubing); here the mixture,

$$SiO_2\ 69\%,\ Na_2O\ 13\%,\ K_2O\ 7\%,\ CaO\ 7\%,\ Al_2O_3\ 4\%,$$

which is rather rich in alkali-metals, is suitable. Excess of alkali-metals, however, is disadvantageous in one respect, because it renders the glass hygroscopic, and comparatively soluble.

In very general demand is a glass of high softening-point and very low coefficient of expansion; such a glass should resist sudden changes of temperature without cracking. The presence of borates in glass helps to bring this about; and zinc is also added to glass for the same purpose. Thus Jena laboratory glass contains approximately

$$SiO_2\ 65\%,\ BaO\ 12\%,\ Al_2O_3\ 4\%,\ B_2O_3\ 15\%,\ As_2O_3\ 3\%,$$

and Jena thermometer glass

$$SiO_2\ 67\%,\ Na_2O\ 14\%,\ Al_2O_3 + Fe_2O_3\ 3\%,\ ZnO\ 7\%,\ MgO\ 7\%,\ B_2O_3\ 2\%.$$

Somewhat similar properties are naturally required for lamp chimneys, and the glass from which these are made often contains boron trioxide,

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[1] See also results of tests by J. D. Cauwood and W. E. S. Turner, *J. Soc. Glass Tech.* **2** (1918), 219.

$$SiO_2\ 66\%,\ Na_2O\ 6\%,\ B_2O_3\ 24\%,\ Sb_2O_3\ 4\%.$$

The manufacturer of optical instruments desires to have at his disposal glasses corresponding to any refractive index which he may happen to require. The heavy elements which are incorporated in glass with a view to raising the refractive index are lead, barium, and sometimes thallium; zinc also raises the refractive index, but to a less extent. Owing to the importance of obtaining just the right qualities in the glass, and of securing maximum transparency and absence of colour, only the very purest materials should be used for optical glasses, and it is naturally manufactured more carefully and in smaller quantities than other glasses. It is usually made in small covered pots, and must be heated until absolutely uniform and free from "seeds." Before the war, 90 per cent. of the optical glass required in this country was imported, largely from Germany. When the supply was cut off, efforts were made by British manufacturers to meet the demand, and in 1918, 95 per cent. of the British consumption was supplied by glass made in the United Kingdom.[1]

Since the refractive index also determines the amount of light reflected at the surface of a glass, it follows that the presence of the elements just mentioned also confers "brilliance" upon a glass; both lead and barium are accordingly added to the batch in manufacturing table glass. "Flint Glass," which is largely used for "hollow ware," sometimes contains

$$SiO_2\ 53\%,\ CaO\ 14\%,\ PbO\ 33\%.$$

A great deal of flint-glass plate is also produced. Many recipes for flint-glass include potassium.

Colour of Glass. A very important matter is the question of the coloration of glass. If the materials of the batch contain iron in the ferrous state, the glass produced will contain ferrous compounds, which will confer on it a deep green colour. In consequence it is customary to add manganese dioxide and potassium nitrate to the charge; the iron is then oxidized to the ferric state, which produces only a pale greenish colour in the glass. The addition of the manganese in the absence of iron would give the glass an amethyst tone roughly complementary to the green due to the ferric iron; consequently the presence of the correct quantity of manganese masks the colour due to the ferric iron, by causing the absorption of light to be non-selective. The masking is more exact if a little cobalt is also added.[1] But although a glass containing ferric iron and also manganese and cobalt may appear colourless, it clearly lets through less light than a similar glass free from all three elements, and therefore for the most transparent glasses iron-free materials should be used.

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[1] *J. Chem. Soc. Ind.* **37** (1918), 356R.

Instead of manganese dioxide, arsenious oxide can be used as a decolorizer; it is usually supposed to act as an oxidizer, being itself reduced to metallic arsenic, which sublimes away in the furnace. This explanation is, however, not universally accepted.[2] Perhaps it acts rather as an oxygen-carrier than an oxidizing agent.

Selenium compounds have also found application as decolorizers, since selenium tends to produce a pink which serves to mask the objectionable green colour referred to above.

Where a **coloured glass** is desired, colouring substances are added in small quantities. The colours produced are in many cases the same as those produced in a borax bead. Green is, as stated above, caused by the presence of iron; rather different shades are obtained by adding chromium or cupric salts to the glass. In the presence of a reducing agent, on the other hand, copper gives to the glass a ruby colour; and a similar tint, rather more bluish in appearance, is obtained by the addition of finely divided gold (such as Purple of Cassius) to glass. Yellow glass is obtained by adding red lead or lead antimoniate or a uranium salt to glass. Under certain circumstances manganese produces a yellow. The brownish colour of the glass often used for beer bottles is connected with the presence of sulphur in the glass; it may be due to sodium polysulphide.[3] This particular glass is impervious to actinic rays, which would cause a deterioration of the beer; a similar glass is used for bottles intended for chemicals, such as silver salts, which are sensitive to light.

The presence of cobalt imparts a blue colour, whilst the addition of manganese dioxide with potassium nitrate causes a violet tint due to manganic compounds; the tint is often seen in old window-glass, containing manganese, which, although originally colourless, has through long exposure to light acquired a violet colour. Ultra-violet light is particularly potent in bringing about the coloration; it can be produced quite quickly by means of a mercury vapour lamp.

It is noteworthy that in some cases the desired colour is not produced if the glass is cooled quickly. In the case of the ruby glass made with gold, the colour is only produced after the glass has been maintained at an elevated temperature for a certain time; exposure to heat for too long a period, however, spoils the colour, rendering it violet or even blue. Here it is certain that we have to deal with a colloidal solution of gold in glass, the gold particles being visible under the ultra-microscope.[1] The colour of the ruby glass is just the same as the colour of the ruby colloidal solutions of gold in water, and the change from red to violet and blue is analogous to the change which occurs in the colloidal solutions upon the addition of sodium chloride. Possibly the gold in the glass when first made is in the combined condition; hence the glass is colourless. On heating, reduction to the metallic state occurs, the ruby tint being due to the colloidal particles of gold; but continued heating causes them to join together to form particles of larger size, and a blue tint is the result. Copper in the presence of reducing agents also produces a fine ruby colour; here also the metallic particles causing the coloration can be made to grow by continued heating. The glass consequently becomes bluish, but if the process is continued long enough the copper particles may become flakes of visible size, causing a "shimmering" appearance in the glass, which is then known as "aventurine." Selenium also gives a red tint to glass, but here again the colour varies with the conditions of preparation.

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[1] S. R. Scholes, *J. Soc. Chem. Ind.* **35** (1916), 518.

[2] See F. Gelstharp, *Trans. Amer. Ceram. Soc.* **15** (1913), 585, who says that arsenious oxide, in the batch, plays the part of a reducing agent.

[3] P. Feneroli, *Koll. Zeitsch.* **16** (1915), 53.

It seems likely that the coloration produced in glass by silver, platinum, iridium, selenium, tellurium, sulphur, carbon, and by lead antimoniate—like that produced by gold and copper—is due to the presence of particles of colloidal size.[2] But the colours produced by the presence of chromium, manganese, cobalt and (in most cases) iron are of a different character, the glasses being "optically empty" (i.e. homogeneous). The colours in these cases may be regarded as due to coloured silicates of the metals in question, and it is noteworthy that the colour frequently agrees with that shown in a concentrated aqueous solution by the ordinary salts of the metal in a corresponding state of oxidation.

When a colourless glass contains colourless particles of microscopic or ultra-microscopic size, having a different refractive index to that of the glassy ground-mass, a non-transparent but translucent material is produced. "**Milk glass,**" required for lamp shades, thermometer scales and similar purposes, can be made by adding fine bone ash (calcium phosphate) to glass. "**Alabaster glass**" is rather similar, but contains a smaller quantity of opacifier.

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[1] H. Siedentopf and R. Zsigmondy, *Ann. Phys.* **10** (1903), 1; J. C. M. Garnett, *Phil. Trans.* **205** [A] (1905), 237.

[2] W. D. Bancroft, *J. Phys. Chem.* **23** (1919), 603.

Barium sulphate is also occasionally used as an opacifier. In many cases the glass produced is clear at high temperatures, since the substance is soluble in the hot mixture. It becomes cloudy when cooled, owing to the separation of the opacifier in minute crystallites. In general, a species of milk glass will always be produced if the composition of the glass is so regulated that a partial devitrification can take place on slow cooling; the minute crystallites formed in the glass act as the light-scattering particles.

" **Opal glass** " is usually produced by adding cryolite (sodium aluminium fluoride) to the batch mixture. Here again the glass produced is clear at high temperatures, but " strikes opal " when it is cooled.[1] The light-scattering particles are often assumed to be simply crystals of cryolite which have separated out on cooling, but there seems to be no certain information on this point.[2]

An " **Enamel** " is a glass made opaque with a suitable opacifier such as cryolite, tin oxide (SnO_2), antimony oxide (SbO_2), or titanium oxide (TiO_2). When hot, it must possess a consistency suitable for coating iron saucepans, plates and the like; and when cold, it must harden to a durable material, which will serve to protect the iron from rust. The mixture used nearly always contains borax, which seems to increase the fusibility.

Soluble Glass.[3] Only the silicates of the alkali metals are appreciably soluble. Silicates such as Na_2SiO_3 are known as definite crystals of constant composition which dissolve in water without trouble. Commercial " water glass," however, contains much more silica than would correspond to such a formula, and is not a definite chemical compound. Owing to the high silica content it can only be brought into solution by rather drastic treatment. It is made by heating sand with sodium carbonate, or with a mixture of sodium sulphate and coal, in a tank furnace. The fused mixture is allowed to drop into cold water, after which it can be powdered with ease. It is brought into solution by treatment with superheated steam under 5 atmospheres pressure; the solution can then be concentrated by evaporation, becoming stiff and treacly. It is usually coloured brown or dark grey by the iron present. The solution is used for impregnating wood, which it thereby renders proof against fire or decay, and for covering stone, which is made watertight. Presumably the silicate is rapidly converted to insoluble silica in the pores of the material by atmospheric carbon dioxide. Various compositions of water glass and asbestos are employed in building. Sodium silicate is also used as a filler in the manufacture of soap.

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[1] Sir H. Jackson, *J. Roy. Soc. Arts*, 68 (1920), 134.

[2] Compare the views of J. G. Smull, *J. Soc. Chem. Ind.* 34 (1915), 402.

[3] R. M. Caven, *J. Soc. Chem. Ind.* 37 (1918), 63T; O. Maetz, *Chem. Zeit.* 42 (1918), 569, 582; W. Pukall, *Ber.* 49 (1916), 397.

It is noteworthy that if the product made in the tank furnace is powdered and heated with a *small* quantity of water for four hours at 70° to 100° C., the particles of the powder unite to form a tough vitreous mass, which dissolves comparatively readily in water without the treatment with superheated steam. This behaviour, which, besides its technological importance, is of considerable theoretical interest, deserves further investigation.

POTASSIUM

Atomic weight 39·10

The Metal

The general resemblance between potassium and sodium is very much closer than the resemblance between sodium and lithium. Nevertheless, the changes observed on passing from lithium to sodium occur again, for the most part, on passing from sodium to potassium. Potassium is more fusible, more volatile and more reactive than sodium. The melting-point is 62·5° C., and the boiling-point 758° C., the vapour having a distinct green colour. But whilst sodium is heavier than lithium, potassium is lighter than sodium, the specific gravity of potassium being 0·86.

The bright silvery lustre of the newly-cut surface of potassium is quickly lost on exposure to damp air; the metal is always kept immersed in oil. Potassium decomposes water with such evolution of heat that the metal melts and the hydrogen produced becomes ignited; in popular language, potassium "catches fire" when thrown on to the surface of water. The metal burns in ordinary air with a violet flame; the same colour may be shown by introducing a potassium compound into a colourless gas-flame.

Laboratory Preparation. The metal can be obtained by electrolysis of fused potassium hydroxide, the operation being carried out in the same way as the preparation of sodium. A thermal method of producing potassium consists in heating potassium hydrogen tartrate first gently and then strongly. During the gentle heating, the tartrate decomposes, leaving a porous mass of intimately mixed potassium carbonate and carbon. If this mixture is heated at a high temperature in a closed iron bottle, the mouth of which is connected to an iron condenser having a large cooling surface, the endothermic reaction

$$K_2CO_3 + 2C = 2K + 3CO$$

occurs; the potassium vapour distils out, and may be condensed and collected under rock oil. Potassium prepared in this way often contains a small amount of a compound of potassium and carbon monoxide, having the composition indicated by the formula $C_6O_6K_6$; this compound, which is structurally related to benzene, is extremely explosive. Potassium obtained thermally is therefore more dangerous to handle than the electrolytic product; the former usually explodes, instead of burning quietly, when introduced into water.

Compounds

Potassium **hydroxide** (*caustic potash*), KOH, is the substance formed when potassium reacts with water; but it can be obtained more conveniently from the carbonate by the action of lime, in the same way as caustic soda, which it closely resembles. It is a hard, white substance, readily deliquescent and capable of absorbing moisture and carbon dioxide from the air. The compound is very soluble, the solution being strongly alkaline. When heated, it melts, and finally volatilizes without losing the combined water. The anhydride, potassium **oxide**, K_2O, can, however, be prepared by the action of potassium on the hydroxide.

The **salts** are prepared by methods analogous to those used in obtaining the sodium salts, and, like the latter, are, in most cases, colourless crystalline substances. In several cases, however, they are distinctly less soluble than the corresponding salts of sodium.

The **chloride** (KCl), **bromide** (KBr) and **iodide** (KI), like the corresponding sodium compounds, crystallize in cubes; a solution of the iodide, which is extremely soluble, has the power of dissolving elemental iodine, a red-brown liquid being obtained. By evaporating this liquid over sulphuric acid, dark crystals of a **tri-iodide**, KI_3, have been obtained.

The **sulphate,** K_2SO_4, crystallizes without combined water in rhombic crystals which might easily be mistaken for crystals belonging to the hexagonal system. The **bisulphate,** $KHSO_4$, loses water when fused, and an anhydride, sometimes known as the **pyrosulphate,** $K_2S_2O_7$, is left.

$$2KHSO_4 = H_2O + K_2S_2O_7.$$

This last-named salt dissolves in water with the evolution of much heat, the bisulphate being regenerated.

The **sulphites,** K_2SO_3 and $KHSO_3$, are prepared just as the corresponding sodium sulphites. An anhydride of the second salt is known in the solid state, and is called potassium **metabisulphite,** $K_2S_2O_5$. It is formed when sulphur dioxide is passed into a hot saturated solution of potassium carbonate, whilst the ordinary bisulphite, $KHSO_3$, is isolated by adding alcohol to a caustic potash solution saturated with sulphur dioxide; the alcohol decreases the solubility of the salt and thus causes its separation. All the sulphites tend to take up oxygen, when exposed to the air.

It is believed that potassium metabisulphite is less susceptible to atmospheric oxidation—and is therefore more suitable for use in the laboratory—than other sulphites.

Potassium nitrate (*nitre* or *saltpetre*), KNO_3, is a colourless salt crystallizing in beautiful long rhombic crystals. It is much more soluble in hot water than in cold, and melts at 339° C. Potassium nitrate is a strong oxidizer, and a fragment of carbon or sulphur brought into contact with the fused salt is oxidized with explosive violence. If nitre be heated still more strongly, it evolves oxygen, the nitrite being produced.

The nitrate of potassium is more easy to crystallize, and thus to obtain pure, than that of sodium; the same statement applies to **potassium chlorate,** which has a comparatively low solubility at low temperatures. For this reason the potassium salts are preferred for use in the laboratory where a pure nitrate, or a pure chlorate, is required.

The **carbonates** (K_2CO_3 and $KHCO_3$), **phosphates** and **sulphides** (K_2S and KHS) are generally similar to the corresponding sodium salts. In each case, the normal salt reacts alkaline, owing to hydrolysis, the acids in question being very weak. Anhydrous potassium carbonate is hygroscopic and very soluble in water; various hydrates are known.

Potassium cyanide, KCN, is a very soluble, easily fusible and extremely poisonous salt, solutions of which are strongly alkaline, and which have powerful reducing properties. It has the power of forming complex salts with the cyanides of heavier metals, and some of these complex cyanides are of great importance. For instance, when potassium cyanide is added to a solution of silver nitrate, a precipitate of silver cyanide is first formed; but the precipitate dissolves in excess of potassium cyanide, forming potassium silver cyanide (KCN.AgCN), which appears to ionize as a complex salt, $K[Ag(CN)_2]$. The most remarkable of the complex cyanides are those formed with the cyanides of iron; these are known as

Potassium ferrocyanide . $4KCN.Fe(CN)_2$ or $K_4Fe(CN)_6$
Potassium ferricyanide . $3KCN.Fe(CN)_3$ or $K_3Fe(CN)_6$

They form well-developed crystals, yellow and brown-red respectively; the solutions possess quite distinct properties from those of simple iron salts, and by precipitation with salts of heavy metals, insoluble ferrocyanides and ferricyanides are obtained. These compounds will be considered further in the section devoted to iron (Vol. III).

In the presence of air, potassium cyanide acts as a solvent for metals like gold, which are undissolved by acids. This property, which also appears to be connected with the formation of complex salts, has been discussed in Chapter XIV (Vol. I).

It has been remarked that potassium cyanide is a powerful reducing agent; when a mixture of dry potassium cyanide with the oxide of any metal standing on the "noble" side of nickel in the potential series is heated, the metal is reduced to the elementary state; the oxygen is abstracted by the cyanide, which becomes converted to the cyanate. The reduction of litharge to metallic lead when heated with potassium cyanide may be represented,

$$PbO + KCN = Pb + KCNO.$$

Similarly some sulphides are reduced to the metallic state by heating with potassium cyanide, which, in this case, passes into the thiocyanate ($KCNS$).

Potassium cyanate, $KCNO$, has been mentioned above, as being prepared by the oxidation of the cyanide; it can conveniently be obtained from potassium ferrocyanide, by fusing it with an oxidizing agent such as potassium dichromate. The cyanate is dissolved out from the fused mass with alcohol. It forms very soluble transparent crystals.

Potassium thiocyanate, $KCNS$, is formed when the cyanide and sulphur are heated together, and is also a soluble deliquescent salt. It gives a red coloration, due to ferric thiocyanate, when added to a solution of a ferric salt.

Certain salts of potassium containing heavy metals in the anion, such as the **dichromate,** $K_2Cr_2O_7$, and **permanganate,** $KMnO_4$, will be described in connection with the heavy metals in question. Both of these salts are more familiar to us than the corresponding sodium compounds, because they are less soluble and crystallize better. One salt of this class does, however, deserve special mention, because it is one of the least soluble potassium compounds known. This is the **platinichloride,** $2KCl.PtCl_4$ or K_2PtCl_6. It is formed as a yellow crystalline precipitate when potassium chloride and platinic chloride are brought together in solution. The platinichloride appears to be a complex salt, ionizing in accordance with the formula $K_2[PtCl_6]$. Although slightly soluble in water, it becomes practically insoluble if alcohol is added to the solution. In this respect potassium differs from sodium, the platinichloride of which is fairly soluble.

Other sparingly soluble salts of potassium are referred to below in the section on analysis.

Analytical

Most potassium compounds confer a violet colour upon the Bunsen flame, but, if much sodium is present as an impurity or otherwise, the colour is likely to be masked. On examination with a spectroscope, however, the observation of a characteristic line (really a pair of lines close together) situated at the red end of the visible spectrum, and of another line at the violet end, give certain indication of the presence of potassium.

Although the commoner salts of the metal are soluble, there are several reagents which yield precipitates with solutions containing potassium. The most important is platinichloric acid, H_2PtCl_6 (the so-called "platinum chloride"), which yields a yellow crystalline precipitate of potassium platinichloride (K_2PtCl_6). Perchloric acid yields a white crystalline precipitate of the perchlorate ($KClO_4$), whilst silicofluoric acid gives a somewhat gelatinous precipitate of silicofluoride (K_2SiF_6). A solution of sodium cobalti-nitrite in the presence of acetic acid produces a yellow crystalline precipitate, $K_2Na[Co(NO_2)_6]$. Finally, when tartaric acid is added to a solution of a potassium salt, a white crystalline precipitate of potassium hydrogen tartrate comes down upon stirring; it is noteworthy that dihydroxy-tartaric acid, which produces a precipitate with sodium salts, gives no such reaction with potassium.

Methods of separating potassium from other metals, notably sodium, depending upon several of the reactions just mentioned, have been worked out. In every case, however, the solubility limit of the potassium salt thrown down is by no means so low as would be desirable for quantitative work; the comparatively soluble character of the precipitated salt is indeed, in many cases, suggested by the crystalline appearance of the precipitate. The commonest method of separating potassium from sodium is by means of hydroplatinic acid. In order to minimize the loss of potassium owing to the appreciable solubility of the precipitate, a concentrated alcoholic solution of the salt-mixture in which potassium is to be estimated is employed, and considerable excess of the precipitant is used. The precipitate is washed with alcohol, in which it is considerably less soluble than in water. It can then be dried at 100° C., and weighed as K_2PtCl_6. Alternatively it can be dissolved in boiling water, and treated with sodium formate, a reducing agent which throws down metallic platinum as a black precipitate. The platinum can be filtered off, washed and weighed; from the weight of platinum, the weight of potassium equivalent to it is readily calculated.

In the methods given above, it is necessary—in order to attain accuracy—to observe rigidly the conditions of working recommended by experienced analysts.[1] For rough work, an indirect method of determining potassium and sodium in a mixture of the chlorides can be used. A known weight of the mixed chlorides is dissolved, and the chlorine content determined by titration with silver nitrate. Since the chlorine content of a mixture of sodium and potassium chlorides varies continuously with the proportion of the two metals from 47·57 per cent. (in the case of pure potassium chloride) to 60·65 per cent. (in the case of pure sodium chloride), it is possible, from the result, to calculate the amount of sodium and potassium in the mixture. Unfortunately, a small error in the determination of the chlorine causes a relatively large error in the potassium content of the mixture.

TERRESTRIAL OCCURRENCE

Like sodium, potassium is an important constituent of the mixture of molten silicates which exist below the surface of the earth, and of which the igneous intrusive rocks pushed up from time to time are mere samples. In these igneous rocks the potassium has usually separated out as crystals of such complex silicates as,

Orthoclase or potash-felspar . . .	$KAlSi_3O_8$
Muscovite or potash-mica . . .	$H_2KAl_3(SiO_4)_3$

Orthoclase, it will be noticed, is analogous in composition to the soda-felspar (albite) mentioned in the section on sodium. Orthoclase felspar and micas containing potassium are essential constituents of granite; in general, potassium occurs in igneous rocks of the acidic (granitic) type rather than in those of basic composition.

As in the case of sodium, the action of water and, no doubt, carbon dioxide, has, during past ages, been dissolving out potassium from exposed igneous rocks. Much of the potassium dissolved in water, passing through the soil has, however, been retained, being absorbed into the plants growing therein. Plants require potassium for their existence and for that reason less potassium is carried down by the rivers into the sea than would otherwise be the case. Moreover the seaweed, growing around the coast, absorbs a further quantity of potassium salts. In addition, the clay particles which are also carried down by the rivers into the sea adsorb a considerable quantity of potassium; it is probably this adsorption which aids in causing the clay particles to settle on the ocean bed. However this may be, potassium seems to be an essential constituent of clays of marine origin. Usually, when the clays become consolidated into shales and slates, the silicates undergo changes, and minute flakes of mica, containing potassium, are formed; thus the potassium may return to the state of combination in which it existed—to a large extent—in the igneous rocks.

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[1] For details, see Sir W. Crookes' "Select Methods in Chemical Analysis" (Longmans).

It is probably the continuous removal of dissolved potassium by the clay particles which prevents any large accumulation of salts of the metal in the sea; actually ordinary sea-water contains only 0·08 per cent. of potassium chloride, as opposed to 2·7 per cent. of sodium chloride. Even the Dead Sea contains only 1·3 per cent. of potassium salts.

It would evidently require very lengthy evaporation of such waters in order to bring the concentration of potassium salts up to the solubility limit, and it is not surprising to find that deposits of soluble potassium salts are far less widely distributed than those of sodium. The Cheshire salt-fields, for instance, contain little or no potassium, but, at Stassfurt, above the thick beds of "rock-salt," layers of potassium salts occur. Evidently these were only thrown down after the concentration process of the Triassic salt-lake had reached a very advanced stage; according to one estimate, the deposition of the thick rock-salt proceeded for 10,000 years before the formation of solid potassium compounds began. The lowest, and therefore first-formed, potassium bed consists of rock-salt mixed with

Polyhalite . . . $K_2SO_4.MgSO_4.2CaSO_4.2H_2O$.

Above this comes a bed of rock-salt and kieserite (magnesium sulphate) upon which rests the bed which still forms the chief source of the world's potash supply; this bed consists of

Carnallite . . . . $KCl.MgCl_2.6H_2O$

mixed with rock-salt, kieserite and other substances.

Various other potassium compounds occur at Stassfurt, but they seem to have been formed through later changes caused by water percolating through the beds; no doubt, the water dissolved out salts at some points, and then—perhaps during a succeeding dry period—they were redeposited at others. Deposits produced by these secondary changes include

Sylvinite . . . . . $(Na,K)Cl$,
Kainite . . . . . . $KCl.MgSO_4.3H_2O$.

Rather similar deposits to those at Stassfurt occur in Alsace,[1] and in Spain.

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[1] P. Kestner, *J. Soc. Chem. Ind.* **37** (1918), 291T.

One other naturally occurring potassium compound deserves mention; this is:

Alunite, or Alum-stone . . $K(AlO)_3(SO_4)_2.3H_2O$.

It occurs in various volcanic districts, and is apparently a weathering-product of lavas brought about by water containing sulphur dioxide, the latter being probably derived from the weathering of pyrites. Considerable deposits occur in the United States, as well as in Italy and Hungary. For many years it has been regarded as a source of alum, but recently it has attained importance as a source of potassium.

TECHNOLOGY AND USES

Extraction fron Carnallite. Up to 1914, the Stassfurt deposits of carnallite represented the most important source of the world's supply of potassium. The Alsatian deposits, although probably richer in potassium, were comparatively undeveloped at that time, whilst the Spanish beds were not worked at all.

The process of extraction practised at Stassfurt is as follows. The carnallite—which is always found mixed with sodium chloride and magnesium sulphate—is ground and extracted by boiling water containing magnesium chloride, derived from a previous operation, which takes up the carnallite, but leaves the sodium chloride and magnesium sulphate largely undissolved. The clear solution obtained passes to crystallizing tanks where it deposits potassium chloride on cooling. So long as magnesium chloride is not in great excess, the single salt, potassium chloride, and not carnallite, will crystallize out. When nearly three-quarters of the total dissolved potassium has been obtained as chloride, the liquors are concentrated further in vacuum evaporators, and then, on cooling, contain a sufficient concentration of magnesium to deposit "artificial carnallite" ($KCl.MgCl_2.6H_2O$). The artificial carnallite can, however, be decomposed by cold water, the more soluble magnesium chloride being dissolved out, whilst potassium chloride is left behind; the magnesium chloride solution produced can then be used to extract more crude carnallite.

The mother liquors from which the "artificial carnallite" has been deposited are not wasted. They contain bromides of magnesium or sodium, and form an important source of the bromine compounds, which are required in photography, in dyeing and in medicine.

Potassium chloride is very largely used in agriculture; all plants requre potassium, and, unless it is added artificially, the soil often becomes impoverished, and good crops are not obtained. Comparatively crude potassium materials can, of course, be used for putting on the soil. It is, however, preferable that the fertilizer employed should not contain much magnesium, excess of which is harmful; the crude mineral kainite, in spite of its magnesium-content, is still used very largely as a fertilizer, but it is better to use potassium chloride, freed from magnesium by the process just described.

In addition to employment in agriculture, the purer forms of potassium chloride are used in the preparation of other potassium compounds, such as the carbonate (which is required in the glass industry) and the nitrate (which is employed in the match industry).

Emergency Sources of Potassium. Naturally when in 1914, the German supplies of potassium were cut off, a somewhat serious position arose in non-German countries, which were forced to fall back on their own resources of potassium. Fortunately, owing to the wide distribution of the element, it was possible—by different processes—to obtain a sufficient supply for the period of the war; and, although the soil of this country was, at the termination of hostilities, considerably "potash-starved," the crops had not suffered in the way that was at one time feared. The demands of the glass-industry had also been met, although the requirements of potash for the glass-makers were rendered more urgent by the fact that the types of glass which contain potassium were, previous to the war, largely imported from Bohemia and Germany. Actually many of the "emergency" processes of obtaining potassium used during the war had been worked previously, to a small extent, but attained sudden importance on the outbreak of hostilities.[1]

Vegetable Sources. Since all plants absorb potassium, the carbonate is one of the main constituents of plant ashes. Many centuries ago, the ashes of wood represented the principal source of potash. Now timber is in most places too valuable to be burnt for this purpose, although in America a great deal of potash is still made from wood ashes. On the other hand, seaweed, being otherwise without value, constitutes a much more hopeful source of potash. Some varieties contain more than others; the ash of the rock weed known as "sea-lettuce" contains 45 per cent. of potassium chloride. The seaweed-burning industry is a very old one on the west coast of Scotland, although shortly before the war it was the iodine, rather than the potassium, of the ash ("kelp")[2] which was of value. During the war, the industry was revived to a large extent, the kelp being used as a source of potash. The method employed is still crude and wasteful; an appreciable amount of potash is volatilized during the burning, whilst a further quantity is apt afterwards to be washed away by the rain.

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[1] See C. G. Cresswell, *J. Soc. Chem. Ind.* **34** (1915), 387.

[2] In America, "kelp" means seaweed; in this country it means seaweed ash.

A kelp industry sprung up during the war on the Pacific coast of America, both in British Columbia [1] and in California.[2] The amount of potash which could be produced annually from the immense areas covered by seaweed is estimated as being five times the whole output of Germany.[3]

Before leaving the subject of the manufacture of potassium from plant sources, it is necessary to refer to the fact that much potassium carbonate is prepared in countries where sugar-beet is grown by the burning of the beet refuse and of the residue from the molasses. This is not really a source of potash, but only the partial recovery of potash previously expended on the soil. It requires much more potash to grow a crop of beet than will ever be recovered from the residues of that crop.

Animal Sources. Another source of potassium is sheep's wool. The natural grease of the sheep contains numerous fatty acids (stearic, palmitic, oleic, etc.), together with a substance called "suint" which consists principally of the soluble potassium salts of the acids. When the wool is washed, these salts pass into solution, and it is possible, by evaporating the water and calcining the residue, to obtain potassium carbonate. The recovery from the greasy solution, however, introduces difficulties, and the product is liable to be of bad quality; the process is not largely practised.[4]

Alunite as a Source.[5] The amount of potash obtained from vegetable and animal sources in the early part of the war being quite unequal to the demand, efforts were made to supplement it from mineral sources. Since supplies of the freely soluble salts were not available, attention was turned to alunite, the basic sulphate of potassium and aluminium. Both in America and also in Australia an industry sprung up in which the alunite was roasted about 750° C., soluble potassium sulphate and insoluble alumina being produced; the former was extracted by leaching.

Felspar as a Source. The problem of extracting potassium from the various rock-forming silicates, such as potash-felspar, has also been considered. Various methods of decomposing felspar are known; one consists in heating it with lime and water under high pressure.[1] Potassium hydroxide can afterwards be extracted from the mass.[1]

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[1] *J. Soc. Chem. Ind.* **36** (1917), 710.

[2] J. W. Turrentine, *Met. Chem. Eng.* **16** (1917), 196.

[3] T. H. Norton, *U.S. Comm. Rep.*, No. 137 (1915), p. 1166.

[4] K. M. Chance, *J. Soc. Chem. Ind.* **37** (1918), 222T. Compare E. V. Chambers, *J. Soc. Chem. Ind.* **40** (1921), 102R.

[5] *J. Soc. Chem. Ind.* **37** (1918), 239A; **40** (1921), 407R.

Recovery from Blast-Furnace Dust.[2] Although it is only profitable, under exceptional conditions, to "mine" and crush felspar or similar minerals as sources of potassium, yet it happens that the ordinary charges introduced into the blast-furnace during the manufacture of cast-iron always contain an appreciable amount of potassium silicate minerals as impurities in the coal and the ore. It has for some time been known that the dust carried off by the exit gases contains notable amounts of potassium. In the absence of chlorine, this comes over largely as the volatile cyanide, and collects as potassium cyanide and potassium carbonate which are minor constituents of the flue-dust. But, when potassium compounds became scarce during the war, an improvement was introduced in this country by adding small amounts of sodium chloride to the blast-furnace charge; it was found that the potassium then comes over almost entirely as chloride and the amount is notably increased. The quality of the cast-iron produced in the furnace does not suffer.

From the dust produced, the soluble potassium chloride can be extracted by leaching, and converted, when required, into other potassium salts. The process was worked in England during the war with great success at a number of blast-furnaces, and enabled the glass-makers to obtain the materials which they required.[3] Since the furnace gases are employed to drive the engines that provide the motive power for the iron-works, the removal of the dust from the gases is very beneficial to the engines. A similar process of potash-recovery has been put into operation at iron-works in America.[4]

One of the best methods of separating the lighter dust from the gas is by the **electrostatic process.**[5] In this process, the dusty gases pass through a series of vertical tubes in the centre of each of which hangs a vertical chain carefully insulated from the tube, and maintained at a very high negative potential (often 60,000 volts). The dust particles become negatively charged in the neighbourhood of the suspended chain, which is constantly giving off electrons, and the particles are then violently attracted to the surface of the positively electrified tube; the powder collecting against the surface of the tube finally falls into a hopper below.

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[1] W. H. Ross, *J. Ind. Eng. Chem.* **9** (1917), 467. Another process is described by A. S. Cushman and G. W. Coggershill (abstract, *J. Soc. Chem. Ind.* **34** (1915), 79).

[2] E. C. Rossiter and C. S. Dingley, *J. Soc. Chem. Ind.* **38** (1919), 375T; R. A. Berry and D. N. McArthur, *J. Soc. Chem. Ind.* **37** (1918), 1T.

[3] See *J. Soc. Chem. Ind.* **39** (1920), 243R.

[4] *J. Soc. Chem. Ind.* **36** (1917), 327.

[5] W. W. Strong, *Trans. Amer. Electrochem. Soc.* **31** (1917), 415; H. D. Braley, *Trans. Amer. Electrochem. Soc.* **35** (1919), 199; H. J. Bush, *J. Soc. Chem. Ind.* **41** (1922), 21T.

Recovery from Cement-works Dust.[1] It has also proved possible to obtain potassium compounds from the dust carried by the gases emerging from a cement-kiln, the dust being caught by means of an electrostatic precipitation plant or in some other way. Salts of potassium can be recovered by leaching this dust with water. The potassium may have come over as some volatile salt (e.g. chloride); but since the gases from the kiln invariably contain oxides of sulphur, the potassium is actually found in the dust partly as sulphate (K_2SO_4), and partly as a double sulphate of potassium and calcium; the potassium present as double sulphate is likely to be left undissolved unless hot water is used for the leaching. As in the case of blast-furnace dust, it is found that the addition of salt or fluorspar to the charge greatly improves the yield of potassium, which then volatilizes as chloride or fluoride. The process has been developed largely in America, although more recently it has been installed at a cement-works in England.[2]

It is generally considered that the blast-furnace process is more remunerative in England, and the cement-kiln process in America. It has been stated that if the dust could be collected from every blast-furnace in this country and properly worked up, the total British requirements of potash could be met from this source alone.[3] It is, however, possible that both recovery processes may prove unable to compete with the product of the carnallite deposits.[4] Germany is recommencing to export potassium salts, and undoubtedly the Alsace deposits, now in the hands of France, will, in future, yield very large amounts of the fertilizer. In the Alsace deposits, the mineral is mainly sylvinite, and, containing comparatively little magnesium, can be applied to the soil without previous refining.

Potassium Carbonate. Although the chloride is a suitable salt for agricultural purposes, it is—both on account of its volatility, and in other respects—unsuited as a source of potassium in glass-making. It has, therefore, to be converted to carbonate. Solvay's process, excellent for making sodium carbonate, would not serve for making the potassium salt, on account of the high solubility of potassium bicarbonate. The "magnesia process" depending on the insolubility of the double carbonate, $2KHCO_3.MgCO_3.4H_2O$ is largely used in Germany. When a cold solution of potassium chloride is treated with magnesium carbonate and carbon dioxide, the compound mentioned comes down as a crystalline precipitate. If heated under pressure at 140° C., this double salt loses the carbon dioxide, and yields soluble potassium carbonate, mixed with the nearly insoluble magnesium carbonate. The product is leached, and filtered, the insoluble magnesium carbonate being used again; from the filtrate, potassium carbonate can be obtained by crystallization.

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[1] W. H. Ross and A. R. Merz, *J. Ind. Eng. Chem.* 9 (1917), 1035; E. Anderson and R. J. Nestell, *J. Ind. Eng. Chem.* 9 (1917), 253; J. Treanor, *Met. Chem. Eng.* **16** (1917), 701; C. Krarup, *Met. Chem. Eng.* **25** (1921), 316.

[2] *J. Soc. Chem. Ind.* **39** (1920), 276R.

[3] K. M. Chance, *J. Soc. Chem. Ind.* **37** (1918), 313R.

[4] Compare P. G. H. Boswell, *J. Soc. Chem. Ind.* **38** (1919), 198R.

Besides its employment in glass-making, potassium carbonate is the source of many other potassium salts.

Potassium hydroxide (*caustic potash*) can be made by the electrolysis of the chloride solution, or by causticizing the carbonate with lime; both processes are similar to those used in preparing caustic soda. It was at one time largely employed for making soft soap, the potassium salts of fatty acids being always softer than the corresponding sodium compounds. But the shortage of potassium compounds has tended to confine the use of potassium soaps to very special purposes.

Other Potassium Salts. In all cases where a potassium and a sodium salt would serve the same purpose equally well, the sodium compound, being cheaper, will be used. In several cases, however, the potassium salt is less soluble than the corresponding sodium compound, and can therefore be obtained purer; moreover potassium salts often absorb moisture less readily, and tend to cake less. The superiority of the potassium compound is seen best in the case of the nitrate, chlorate, perchlorate, dichromate and permanganate, all of which are made and used on a large scale.

Potassium nitrate (*saltpetre, nitre*) is obtained by interaction of hot concentrated solutions of potassium chloride and of sodium nitrate (Chili saltpetre). The double decomposition

$$NaNO_3 + KCl = NaCl + KNO_3$$

occurs. Sodium chloride is, at high temperatures, more insoluble than the other salts present and separates out. The mother liquid is filtered hot, and run into crystallizing tanks where potassium nitrate (which, although very soluble in hot water, is much less soluble in cold) separates on cooling. It is purified by recrystallization.

Potassium nitrate is used largely at the glass-works; in the making of flint glass, it is added as an oxidizing agent to the batch, to prevent lead from becoming reduced to the metallic state. The salt is also useful in the curing of meat, to which it imparts a red colour. It is employed in fireworks, and is a constituent of old-fashioned black gunpowder.

Potassium chlorate was at one time prepared by passing chlorine into warm caustic potash solution

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

But, since this reaction reconverts five-sixths of the potassium hydroxide into chloride, from which the hydroxide was originally derived, the method has been altered. Chlorine is, accordingly, passed into hot milk of lime, calcium chlorate being formed by the analogous reaction,

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

Since lime is a much cheaper alkali than caustic potash, the conversion of part of it to calcium chloride is not serious. The excess of lime is allowed to settle, and the clear liquid is run off into tanks, and mixed with the equivalent quantity of potassium chloride. Double decomposition takes place, and potassium chlorate, which at low temperatures is very much less soluble than the other salts present, crystallizes on cooling as a glittering mass. It can be purified by recrystallization.

Milk of magnesia is often used in the place of milk of lime, because the solubility of potassium chlorate in the presence of magnesium chloride happens to be less than the solubility in the presence of calcium chloride. The process is conducted in a method similar to the lime process, but it is usual to remove some of the magnesium chloride from the liquid, by evaporation, before potassium chloride is added.[1] It may, perhaps, be of interest to mention that the liquors from which potassium chlorate, and other highly oxidized salts, are crystallized on an industrial scale, have in practice a very pronounced purplish-pink colour. This was attributed at one time to the presence of a trace of permanganate or to the oxide Mn_3O_4, but it is now thought to be due, in most cases, to an iron compound.

Electrolytic Production of Potassium Chlorate. The chlorate may also be made by the electrolysis of potassium chloride solution. Where the products of the electrolysis are kept apart by means of a diaphragm, caustic potash and chlorine are obtained, and this is, of course, the most important way of preparing caustic potash. Where there is no diaphragm, the products react forming potassium hypochlorite and chloride, if the liquid is cool,

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[1] C. L. Higgins, *J. Soc. Chem. Ind.* 6 (1887), 248.

$$2KOH + Cl_2 = KOCl + KCl + H_2O.$$

But, if the solution is warm, and especially if it is slightly acid before the electrolysis begins, the hypochlorite, even if first formed, quickly decomposes, yielding the chlorate. The reaction[1] may be written simply

$$3KClO = KClO_3 + 2KCl.$$

No doubt, a part of the hypochlorite first produced may be oxidized to chlorate electrolytically at the anode. It is advisable to allow the liquid full access to the anode, and to avoid the production of any protective film on that electrode. On the other hand, contact with the cathode leads to destruction of hypochlorite and chlorate alike, and it is therefore beneficial to add to the solution a little chromate, which forms a protective film on the cathode—as was explained in the section on sodium hypochlorite. It has also been found desirable that the original chloride solution employed should be made slightly acid before electrolysis starts. In this case, it remains acid in the neighbourhood of the anode throughout the process, and the stability of hypochlorite in presence of acid being small, its decomposition into chlorate and chloride is favoured. Moreover unless the solution around the anode is acid, much current is wasted upon the evolution of oxygen. This may be due in part to the discharge of hydroxyl ions, but is mainly to be attributed to the discharge of hypochlorite ions (OCl)'. Both kinds of ions occur to a much greater extent in an alkaline solution than in the presence of an acid, since hypochlorous acid itself is a weak acid, only slightly ionized; if therefore the bath is kept weakly acid, the loss of efficiency due to oxygen-production is reduced to a minimum.[2]

Chlorates are made in Germany by electrolysis on a large scale. The chloride solution containing a little potassium bichromate (which serves not only to produce a film on the cathode, but also to render the solution slightly acid) flows through a cell containing parallel electrodes; before the war both electrodes were frequently made of platinum-iridium gauze, and it is stated that even at the present time no satisfactory substitute for platinum as the anode material has yet been found.[3] The temperature employed is said to be kept about 40° C. After the treatment, the liquor passes into crystallizing tanks where potassium chlorate is deposited on cooling. In practice, it is found more economical of potassium to use sodium chloride solution for the electrolysis, and then to decompose the strong solution of sodium chlorate produced with potassium chloride.

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[1] Most writers represent the reaction, which occurs most readily in acid solutions, as an interaction between hypochlorous acid and hypochlorite ions, thus:—$2HOCl + OCl' = ClO'_3 + 2H^\cdot + 2Cl'$.

[2] Compare the views of F. Foerster and E. Müller, *Zeitsch. Elektrochem.* **9** (1903), 195. See also N. V. S. Knibbs and H. Palfreeman, *Trans. Faraday Soc.* **16** (1920), 402.

[3] K. Arndt, *Electrotech. Zeitsch.* **42** (1921), 345.

In an American process which has recently been worked out, it is proposed to use potassium chloride derived from felspar as raw material; it is electrolysed in a cell fitted with carbon anodes, and magnesium cathodes, the liquid being kept acid at the anode and alkaline at the cathode.[1]

Potassium chlorate is used largely in the manufacture of matches. It has also been employed as an oxidizing agent in organic chemistry, but for this purpose the cheaper sodium chlorate is equally effective. Owing to its high oxidizing power, the chlorate is somewhat dangerous to handle on a large scale, and should be kept out of contact with all organic matter.

Potassium perchlorate is manufactured by the electrolytic oxidation of a solution of sodium chlorate; the sodium perchlorate produced is afterwards decomposed with potassium chloride, when the almost insoluble potassium perchlorate is thrown down. It is often stated that a low temperature is required for the electrolysis, but this is apparently wrong. The current efficiency is very high (85–90 per cent.) even at 60° C.; at that temperature the presence of acid appears to be beneficial.[2]

Potassium perchlorate finds employment in the explosive industry. It is more stable than the chlorate, but is nevertheless, owing to the high oxygen content, rather a dangerous substance to handle dry. It must be kept away from all organic matter.

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[1] A. G. Betts, *Met. Chem. Eng.* **15** (1916), 627.

[2] J. G. Williams, *Trans. Faraday Soc.* **15** (1920), Part 3, 134; N. V. S. Knibbs, *Trans. Faraday Soc.* **16** (1920), 424; F. Winteler, *Zeitsch. Elektrochem.* **5** (1898), 50, 217; **7** (1901), 635; W. Oeschli, *Zeitsch. Elektrochem.* **9** (1903), 807; E. Blau and R. Weingard, *Zeitsch. Elektrochem.* **27** (1921), 1.

RUBIDIUM

Atomic weight . 85·45

The Metal

The changes seen on passing from potassium to rubidium are for the most part the same as those observed in passing from sodium to potassium. Rubidium, which is lustrous like silver when fresh but quickly tarnishes in air, is heavier, more easily fusible and more volatile than potassium ; the melting-point is as low as 38° C.

Rubidium is even more reactive than potassium, and like the latter takes fire when thrown on to water. The metal can be prepared from the hydroxide by heating strongly with carbon, or, if preferred, with aluminium, when the volatile rubidium distils off.

Compounds

The **hydroxide,** RbOH, is a deliquescent soluble body, the solution of which is strongly alkaline. The solid is said to have a greyish tinge. The **oxide,** Rb_2O, has not been prepared pure ; the mixture obtained when rubidium is burnt in the air contains Rb_2O mixed with a higher oxide, possibly Rb_2O_4.

Salts. The rubidium salts closely resemble those of potassium. The **chloride, bromide** and **iodide** crystallize in cubes. The nitrate and sulphate are, however, considerably more soluble than those of potassium. The platinichloride is distinctly less soluble than that of potassium, the insolubility of the platinichlorides rising in the group with the atomic weight.

Analytical

Rubidium confers a reddish-violet colour on the Bunsen flame ; the spectrum shows two pronounced lines in the red, to which the element owes its name—it was originally discovered by means of the spectroscope. There are, however, other lines, including two important ones at the violet end of the spectrum.

Like potassium, rubidium is precipitated by platinichloric, perchloric, tartaric and silicofluoric acids ; methods of estimating the metal by means of these reagents have been worked out.

It also yields an insoluble stannichloride, $Rb_2[SnCl_6]$ or $2RbCl.SnCl_4$, which is obtained as a precipitate when a rubidium chloride solution is treated with stannic chloride. A rough method of separating rubidium from potassium depends on this fact.[1]

TERRESTRIAL OCCURRENCE

Rubidium and the succeeding element, cæsium, occur only in very small quantities in the earth and like lithium have tended to accumulate in the acidic—or last-consolidated—portions of igneous rocks; they are found, in fact, in the same minerals as contain lithium. Thus some samples of lepidolite (lithia-mica) have been shown to contain as much as 0·5 per cent. of rubidium and cæsium. The water of some mineral springs—no doubt arising from intrusions comparatively rich in rubidium and cæsium—yield appreciable quantities of the salts of each metal. The potassium salt deposits of Stassfurt also contain rubidium. There is little demand for compounds of rubidium, but it is not difficult to separate it from the mother liquors of the Stassfurt salt industry as the sparingly soluble rubidium alum ($Rb_2SO_4.Al_2(SO_4)_3.24H_2O$).

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[1] W. Feit and K. Kubierschky, *Chem. Zeit.* **16** (1892), 335.

CÆSIUM

Atomic weight 132·81

The Metal

The gradual variation of properties with the atomic weight reaches a culmination in cæsium. This is the most fusible metal of the group, the melting-point being 26° C.; it has the lowest boiling-point (670°), and the highest specific gravity (1·87). It is probably the most reactive metal known. Cæsium catches fire when dropped on to water, and sometimes takes fire spontaneously when exposed for some time to damp air.

The metal can be prepared in the same way as rubidium.

Compounds

The **hydroxide**, CsOH, is very similar to that of rubidium. The normal **oxide**, Cs_2O, has been prepared by the action of oxygen upon excess of cæsium. The excess of the metal can be removed by virtue of its volatility through distillation *in vacuo*; but if the distillation be conducted at too high a temperature part of the combined cæsium will pass away, and a peroxide will be left. The normal oxide, Cs_2O, has an orange colour.

Salts. Cæsium salts resemble the rubidium salts. The **chloride,** which crystallizes in cubes, is, however, deliquescent, and more volatile than rubidium chloride. The **platinichloride** is more insoluble than that of any other metal of the group.

Analytical

Cæsium is usually detected by means of the spectroscope; there are several lines, the two most pronounced lines being in the blue region (hence the name "cæsium," derived from the Latin word, Cæsius, blue-grey). In the absence of other metals, cæsium salts confer a red-violet colour upon the flame.

Cæsium salts, like those of potassium and rubidium, yield precipitates with platinichloric, perchloric, tartaric and silicofluoric acids. Like rubidium, it is precipitated, as a double salt, by tin chloride, and—by means of this reaction—can be separated from potassium.

The separation from rubidium can be carried out by various rather laborious processes, depending on the slight differences in the solubility of the bitartrates or platinichlorides. Another method depends on the fact that the addition of a solution of antimony chloride dissolved in hydrochloric acid causes the precipitation of cæsium as the double salt $SbCl_3.CsCl$, whilst rubidium remains in solution; the precipitation, however, appears to be incomplete.

TERRESTRIAL OCCURRENCE

As mentioned in the section on rubidium, cæsium occurs along with the former metal, in small amounts in various minerals, such as lepidolite. A very rare silicate mineral, called "pollux," contains a considerable quantity of cæsium; samples from Elba have been found to contain 34 per cent. Cæsium occurs in traces in some mineral waters. On the whole, it is less abundant than rubidium. It has found no practical application, and consequently there is no technology.

AMMONIUM

Before leaving Group IA, it is necessary to refer to the striking connection between the salts of the alkali metals and the salts obtained when ammonia combines with acids. When an aqueous solution of ammonia acts upon an equivalent quantity of an acid, the solution produced is found to contain crystalline salts, known as *ammonium salts*. The same bodies are obtained when ammonia gas is allowed to react with acidic oxides or hydrogen halides. Thus ammonia combines with hydrogen chloride to give ammonium chloride, NH_4Cl. Now it is found that many ammonium salts are not only similar in constitution to the salts of the alkali metals, but are actually isomorphous with them. Thus ammonium sulphate $(NH_4)_2SO_4$, is isomorphous with potassium sulphate, K_2SO_4. In all ammonium salts the radicle (NH_4) takes the place of a metal.

It is thought that the hydroxide, NH_4OH, exists in aqueous solutions of ammonia,

$$NH_3 + H_2O = NH_4OH.$$

The alkalinity of solutions of ammonia is commonly attributed to the ionization of this compound, into $(NH_4)^{\cdot}$ and $(OH)'$ ions. But evidently the dissociation is far from complete, for ammonia is a much weaker alkali than potash or soda, and the solutions contain a smaller concentration of hydroxyl ions than caustic alkalis of equivalent strength. The limited hydroxyl concentration in a solution of ammonia renders it a very valuable reagent; metals which have very insoluble hydroxides are precipitated by ammonia, whilst those having slightly more soluble hydroxides remain in solution.

Ammonium salts decompose into ammonia and the acid or oxide when heated. Some, for instance ammonium chloride, appear to sublime unchanged; really, however, the vapour obtained when ammonium chloride is volatilized consists not of unchanged ammonium chloride, but of ammonia and hydrogen chloride. If the vapour be cooled again, these constituents recombine to form solid ammonium chloride,

$$\underset{\text{Solid}}{NH_4Cl} \longrightarrow \underset{\text{Vapour}}{NH_3 + HCl} \longrightarrow \underset{\text{Solid}}{NH_4Cl}$$

But, if the vapour is passed through a tube of porous material which is more pervious to ammonia than to hydrogen chloride, a partial separation of the two constituents is brought about.

Most of the ammonium salts are at ordinary temperatures white crystalline soluble substances, like the salts of sodium and potassium. The **chloride** (NH_4Cl) occurs in fibrous crystalline masses or in arborescent crystal growths, the sulphate [$(NH_4)_2SO_4$] in rhombic crystals isomorphous with the anhydrous sulphates of the alkali metals. The **nitrate** is of special interest, since, on heating, it decomposes into nitrous oxide and water thus

$$(NH_4)NO_3 = N_2O + 2H_2O$$

whilst the **nitrite**, upon being warmed in solution, yields nitrogen

$$(NH_4)NO_2 = N_2 + 2H_2O.$$

Ammonium sulphide $(NH_4)_2S$, and **Ammonium hydrogen sulphide**, NH_4HS, are formed in solution by saturating ammonia solution with sulphuretted hydrogen. The proportion of normal sulphide increases with the strength of the original ammonia. The solution is colourless when first produced, but usually grows yellow when stored, owing to the formation of polysulphides.

Ammonium Carbonates. When an ammonia solution is saturated with carbon dioxide, the **bicarbonate** $(NH_4)HCO_3$ is produced; if an equal quantity of ammonia is then added to the solution, the **normal carbonate** $(NH_4)_2CO_3$ is obtained. The same compound mixed with an anhydride, **ammonium carbamate** $(NH_4)CO_2(NH_2)$ is formed when a mixture of ammonium sulphate and calcium carbonate are sublimed; calcium sulphate is left behind.

Ammonia tends to combine with the salts of many heavy metals, especially those occurring in the centre of the Periodic Table, forming complex salts in which the group NH_3 forms part of the complex cation. Many of these complex salts, such as $[Co(NH_3)_6]Cl_3$; $\left[Co\begin{matrix}(NH_3)_5\\ Cl\end{matrix}\right]Cl_2$; $[Pt(NH_3)_4]Cl_2$; and $[Cu(NH_3)_4]SO_4$, will be referred to in the subsequent volumes of this book.

GROUP IIA

	Atomic Weight.
Beryllium	9·1
Magnesium	24·32
Calcium	40·07
Strontium	87·63
Barium	137·37
Radium	226·0

The metals of the Group IIA are distinctly less reactive than those of Group IA. The electrode potential of the elements, however, becomes more negative as the atomic weight rises, and accordingly the higher members of the group resemble the alkali metals most closely. Likewise, as the atomic weight rises, the basic nature of the oxides, as well as their solubility and affinity for water, becomes more pronounced; thus whilst magnesium hydroxide is only slightly soluble, and feebly alkaline, yielding salts which are hydrolysed in aqueous solution, the hydroxide of barium is far more soluble, and acts as a strongly basic substance. Moreover, whilst magnesium oxide can readily be obtained by heating the carbonate or nitrate, it is much more difficult to prepare barium oxide in the same way. Since the violence of the reaction of water upon a metal depends upon the electrode potential of the metal and also upon the solubility of the oxide or hydroxide formed, it follows that the higher members of the group will decompose water quite violently (barium in fact reacts almost as violently as sodium), while the lower members, like magnesium and beryllium, are only slowly and superficially affected. But it must be noticed that in every case the metals evolve hydrogen from acids with great readiness. All the members of the group have very high heats of oxidation; in every case, the metal burns readily in air. The metals stand too near the negative end of the potential series to be produced by the electrolysis of an aqueous solution.

It will be seen that the higher and more reactive members of the group, calcium, strontium and barium, resemble the first and least reactive member of Group IA, namely lithium, not only as regards the behaviour of the elements, but also in respect of the solubility of the salts. On the other hand, the lower members, beryllium and magnesium, have certain properties in common with zinc, the first metal of Group IIB; many of the salts of magnesium are isomorphous with those of zinc. Beryllium and magnesium are also closely related to aluminium, which falls beside magnesium in the Periodic Table.

The metals of the Group IIA are divalent in their typical compounds. The salts are colourless. Sparingly soluble compounds are much more common than in Group IA. The solubility of the carbonate and phosphate is low; the solubility of the hydroxide is, as already stated, somewhat low in the case of the first members of the group, but becomes greater as we pass, through calcium and strontium, to barium and radium. On the other hand, the sulphates, which are fairly soluble in the case of beryllium and magnesium, become less soluble in the case of calcium and strontium, whilst the sulphates of barium and radium may be regarded for many purposes as "insoluble" substances.

BERYLLIUM

Atomic weight

The Metal

Beryllium (also known as *Glucinum*) is a white metal, rather harder than the metals of the last group, and also somewhat heavier, the specific gravity being 1·793 ; nevertheless it is lighter than any other metal permanent in air, except magnesium. It melts at quite a high temperature (1,278° C.), the "heat of fusion" being larger than that of any other metal.[1] It is malleable, and beads of beryllium flatten easily, when struck with a hammer.

Beryllium evolves hydrogen from dilute hydrochloric acid and from warm dilute sulphuric acid. But beryllium cannot be said to decompose water, presumably because it becomes covered with a protective layer of an insoluble oxide or hydroxide, as soon as any action has taken place. Solutions of caustic soda or potash, reagents which dissolve beryllium oxide, attack the metal readily with evolution of hydrogen. Beryllium is only superficially oxidized when heated in the air ; here again the oxide formed on the surface protects the metal below from further attack. Powdered beryllium, however, takes fire on being heated, burning with a bright flame.

Laboratory Preparation. The metal is prepared by the electrolysis of a mixture of beryllium and sodium fluorides, melted in a nickel crucible, which is used as a cathode, a carbon rod being introduced as anode ; crystals of beryllium appear on the sides of the crucible. An alternative method of preparation is to heat beryllium chloride with some more reactive metal such as sodium. Since beryllium chloride is volatile it is necessary to seal the mixture in a bomb tube prior to heating. This method yields beryllium in small beads containing but little sodium.[2]

Compounds

Beryllium oxide (*beryllia*), BeO, is formed when beryllium is burnt in air. It can also be obtained by igniting the carbonate or nitrate. A hydrated form (usually known as "beryllium hydroxide," $Be(OH)_2$, but possibly not a true compound) is formed as a voluminous gelatinous precipitate when ammonia is added to a solution of any beryllium salt. When freshly precipitated, the hydroxide is readily soluble in acids and alkalis, but if it is kept for any length of time, it undergoes a gradual change, becoming less readily soluble in acids. The "ageing"—as this gradual change is called—is greatly accelerated by boiling the precipitate with water, but occurs at ordinary temperatures when the precipitate is dried.[1] The ageing is probably merely a physical change, the precipitate becoming denser and less gelatinous; the diminished rate of dissolution is due to the diminution in the surface area.

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[1] G. Oesterheld, *Zeitsch. Anorg. Chem.* **97** (1916), 1.

[2] M. A. Hunter, *Eighth Int. Cong. App. Chem.* (1912), II. 134. Compare also *J. Soc. Chem. Ind.* **40** (1921), 314R.

The anhydrous oxide dissolves only very slowly in acids and alkalis owing to the small surface area presented to the liquid. It is indeed possible, by ignition at a high temperature, to convert beryllium oxide into a form so hard and dense as to be practically unattacked by any ordinary reagent. A similar conversion of aluminium oxide into a hard and insoluble form will be met with later. It should be mentioned that ignited beryllia is harder than ignited alumina (corundum), and approaches the hardness of diamond.

Beryllium hydroxide, even in the freshly precipitated form, is so slightly soluble in water that the saturated solution scarcely shows an alkaline reaction. Beryllium oxide differs from the oxides of the alkali metals not only in its indifference to water, but also in its extremely high melting-point. It is an extremely refractory substance, only melting at about 2,525° C.

Beryllium Salts. The salts can be prepared by dissolving the precipitated "hydroxide" in the acids in question; they are all without colour, except where derived from coloured acids. The **sulphate,** $BeSO_4$, usually crystallizes with four molecules of water, although other hydrates have been described. The **nitrate** is deliquescent. The **anhydrous chloride,** $BeCl_2$, is preferably obtained by passing chlorine gas over a heated mixture of beryllium oxide and carbon; the mixture of beryllium oxide and carbon should be made into pellets, and heated in a hard glass tube through which chlorine is passed. This is a general method of making anhydrous chlorides. Beryllium chloride is volatile and has a vapour density corresponding to the formula $BeCl_2$. It is deliquescent, as indeed are all the chlorides of the metals of this group. Various hydrates are known.

The solutions of soluble beryllium salts usually have an acid reaction owing to hydrolysis, and have a sweetish taste; hence the alternative name of the metal—"glucinum."

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[1] F. Haber and G. van Oordt, *Zeitsch. Anorg. Chem.* 38 (1904), 377.

Organic Salts.[1] When beryllium carbonate is treated with excess of formic, acetic, or other fatty acid, curious volatile salts are produced; as a result of analysis and the determination of vapour density, the formulæ $(H.COO)_6Be_4O$ and $(CH_3.COO)_6Be_4O$ have been assigned to the formate and acetate respectively. They are practically insoluble in cold water, but the acetate dissolves readily in chloroform.

Insoluble Salts. When a beryllium salt is precipitated with sodium carbonate, the white precipitate consists of a **basic carbonate.** If this is suspended in water, and carbon dioxide is passed through the suspension, it passes to some extent into solution, the normal carbonate ($BeCO_3$), which is soluble, being formed. The latter substance, however, readily loses carbon dioxide, regenerating the basic salt. Another insoluble salt is the **phosphate,** which is obtained when an alkali-metal phosphate is added to a solution of a soluble salt of beryllium.

Beryllates. A solution of beryllium hydroxide in caustic alkali probably contains a "beryllate," corresponding to the "zincate" formed from zinc oxide. But the solutions are strongly alkaline, and would appear to be considerably hydrolysed. Beryllium hydroxide is readily deposited from the dilute solutions. Many chemists would say that the apparent solvent action of alkalis on beryllium hydroxide is not due to "chemical combination" but to "peptization," a colloidal solution being produced. But, as was pointed out in Chapter VII (Vol. I), the two views are not so irreconcilable as is sometimes supposed.

Analytical

In the solubility of its salts, beryllium resembles aluminium more closely than any member of its own group. It is easily distinguished, and even separated, from most other metals. It gives no precipitate with hydrogen sulphide in acid solution, but it gives an insoluble hydroxide upon the addition of ammonia, which dissolves readily in caustic alkalis. Aluminium behaves in exactly the same way, and the separation of these two elements is less easy. However, by adding 6N sodium hydroxide to a solution containing both metals, until the precipitate of hydroxides just redissolves, diluting the solution and boiling for forty minutes, the whole of the beryllium is reprecipitated as hydroxide, owing to the hydrolysis of the beryllate; sodium aluminate is less easily decomposed and the aluminium remains in solution.[1]

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[1] G. Urbain and H. Lacombe, *Comptes Rend.* **133** (1901), 874; **134** (1902), 772.

Having obtained a solution of a beryllium salt free from other metals, it can be precipitated as hydroxide with ammonia; the precipitate is then filtered off, and, after drying, ignited; if preferred, it can be ignited in contact with the filter paper. The residue is weighed as beryllium oxide (BeO).

TERRESTRIAL OCCURRENCE

Beryllium is one of the rarer elements, but it must have been present to a small extent in the molten masses of silicates which from time to time have been intruded upwards into the earth's crust. Like other rare elements, it has tended—during the solidification of the magma—to accumulate in the portions which remained liquid to the end. Pegmatitic veins, for instance, sometimes contain the silicate of beryllium and aluminium, known as

Beryl . $Be_3Al_2(SiO_3)_6$.

It seems, however, fairly certain that the vapour of beryllium fluoride was also among the gases released from the igneous mass during that last stage of cooling, for we find beryls associated with various other minerals such as tourmaline and topaz, which are known to have been formed by the action of gases containing fluorine and boron.[2]

Where, as in Madagascar, the original igneous rocks containing beryls have become converted into red earths or laterites, the beryls have remained unchanged. Their extraction from such soft materials is, of course, comparatively easy.[3]

Beryl is sometimes colourless, but often contains traces of other metals which cause it to be coloured. A pale green variety is known as "aquamarine," whilst a bright green variety, which owes its colour to the presence of chromium, is called "emerald." Beryls occur in all parts of the world, notably the United States, Madagascar, Brazil, India, and Siberia. The best emeralds come from the Republic of Columbia, where they occur in calcite veins traversing a limestone.[4] These veins were probably caused by the passage of fluoride vapours or fluoride waters—containing a certain amount of beryllium fluoride—through the cracks of the limestone. The calcium carbonate of the limestone has been attacked, and afterwards has been redeposited as calcite, whilst the comparatively small amount of beryllium fluoride has suffered decomposition, the beryllium being deposited as green silicate crystals (emeralds).

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[1] H. T. S. Britton, *Analyst*, 46 (1921), 359. For other methods, see Sir W. Crookes, "Select Methods in Chemical Analysis" (Longmans), 1905 edition, p. 160.

[2] Compare F. H. Hatch, *Trans. Inst. Min. Met.* 21 (1911–12), 203.

[3] G. F. Kunz, *Eng. Min. J.* 111 (1921), 14.

[4] C. Olden, *Trans. Inst. Min. Met.* 21 (1911–12), 193.

Although beryls of the variety suitable for display as gem-stones are comparatively rare, the less choice crystals are far from uncommon. In a few places very big crystals occur. In New Hampshire a particular crystal was found weighing 2,900 lbs.

Another form in which beryllium occurs is the aluminate

Chrysoberyl . . . $BeO.Al_2O_3$

which likewise occurs along with tourmaline in granitic rocks, and is also found as pebbles in deposits which presumably have been derived from such rocks. The simple silicate

Phenacite . . . Be_2SiO_4

is also found in nature.

Another beryllium mineral, which will be mentioned again in the section on the "rare earth metals," is

Gadolinite . . . $Be_2Fe(YO)_2(SiO_4)_2$.

TECHNOLOGY AND USES

Gem-stones. The clearer varieties of beryl, and especially the green variety known as emerald, are considerably sought after as gem-stones. It is perhaps a little curious that the emerald should be prized so highly as a gem, since in the two properties which are generally desired in jewels, namely high refractive index (which causes lustre) and great hardness (which means durability), emerald stands distinctly below most of the other gem-stones. Nevertheless emeralds appear to be one of the most highly prized of stones. The emerald mines of the Republic of Columbia are largely worked, whilst the other varieties of beryl are obtained in many places, notably in the Limousin and in Madagascar. The by-products from the beryl industry form the most important sources of beryllium compounds.

Preparation of Beryllium Salts. In the preparation of beryllium compounds, the less choice and smaller fragments of beryl are employed. Beryl is not an easy mineral to decompose, being practically unaffected by treatment with acids. If very finely powdered, however, beryl is slowly attacked by various mixtures of fused salts; the fine powdering is of importance, as it is essential to produce the maximum surface of contact between the beryl and the solvent. A fused mixture of sodium and potassium carbonates has been used as a solvent, but probably the easiest way of breaking down beryl is to heat the finely divided mineral with sodium silicofluoride (Na_2SiF_6).[1] After heating, the mass is extracted with boiling water, when beryllium fluoride dissolves, silica and aluminium hydroxide being left behind as an insoluble residue, which can be removed by filtration. From the filtrate, beryllium is precipitated as hydroxide by means of caustic soda; the precipitate is then dissolved in sulphuric acid, and by recrystallization, beryllium sulphate can be obtained in a state of moderate purity.

Where gadolinite is the source of beryllium, the powdered mineral can be decomposed most easily with hot concentrated sulphuric acid.[2]

Uses. There are but few technical uses for beryllium compounds. Beryllium nitrate is added to the thorium solution used for the impregnation of gas mantles; the presence of beryllium oxide in the ash skeleton of thoria appears to add to the strength of the skeleton. At the commencement of the war, some difficulty was caused in the mantle industry by the shortage of beryllium salts; the difficulty was soon overcome.[3]

Beryllium-copper alloys are said to have very valuable properties, but their use is restricted by the expense of obtaining beryllium. Owing to the low specific gravity, the question of employing beryllium in light alloys is arousing interest. Were beryllium ores more plentiful, it is likely that beryllia would find employment as a refractory.

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[1] H. Copaux, *Comptes Rend.* **168** (1919), 610. Numerous alternative methods are given by J. S. Negru, *Met. Chem. Eng.* **21** (1919), 353.

[2] C. James and G. A. Perley, *J. Amer. Chem. Soc.* **38** (1916), 875.

[3] S. J. Johnstone, *J. Soc. Chem. Ind.* **35** (1916), 812.

MAGNESIUM

Atomic weight 24·32

The Metal

Magnesium is a white metal, having a brilliant lustre when fresh, although it soon becomes dull in damp air. It is much softer than beryllium, being actually a little harder than tin; magnesium is both ductile and malleable. It melts at 650° C., far below the melting-point of beryllium, and boils about 1,100° C. It is the lightest metal which can be said to be "permanent" in air, lighter actually than beryllium or aluminium, the specific gravity being 1·74.

Magnesium is more reactive than beryllium. It evolves hydrogen with great rapidity even from very dilute acid solutions. On the other hand, it is unattacked by caustic alkalis, and reacts only very slowly with pure water, possibly because the product of the reaction is the hydroxide, which is but feebly soluble and which seems to produce a protective layer over the surface of the metal. Nevertheless, when certain salts are present in the water, hydrogen is freely evolved, and magnesium hydroxide is produced in a form which does not seem to interfere with the continued attack upon the metal.[1] Sodium, potassium and ammonium chlorides are notably effective in promoting the attack of magnesium by water; chlorides of calcium and barium are said to have a less marked action.

Although most of the investigators prefer to ascribe the effect of the chlorides in promoting the corrosion of magnesium vaguely to some "specific catalytic action" exerted by the salts in question, it is possible to suggest a more satisfactory explanation. Ammonium chloride has—as is well known—a considerable solvent power for magnesium hydroxide, and thus it will prevent the formation of a protective film. It is often stated that the same explanation cannot be extended to the case of the other chlorides (e.g. potassium chloride), because when magnesium is attacked by potassium chloride, a copious precipitate of magnesium hydroxide appears. But, although the solvent power of potassium chloride may not be sufficient to prevent the formation of solid magnesium hydroxide entirely, it may be sufficient to modify the character of the hydroxide precipitated; a substance precipitated from a solution in which it is partially soluble usually differs considerably in physical condition from the same substance precipitated from a solution in which the solubility is very low. Furthermore, it is rather to be expected that the presence of chlorides in the solution will tend to "loosen" the hydroxide, causing the compound to enter the body of the solution as a diffuse precipitate, instead of adhering to the surface of the metal as a tight protective film. Any dissolved substance which lowers the interfacial tension between the water and the hydroxide is likely to have this loosening action, and the fact that chlorides are known in many cases to have a peptizing action upon precipitated hydroxides would seem to indicate that chlorides *do* reduce the interfacial tension between the hydroxides and water.[1]

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[1] L. Kahlenberg, *J. Amer. Chem. Soc.* **25** (1903), 380; C. F. Roberts and L. Brown, *J. Amer. Chem. Soc.* **25** (1903), 801; F. H. Getman, *J. Amer. Chem. Soc.* **38** (1916), 2594; **39** (1917), 596; W. Hughes, *Trans. Chem. Soc.* **115** (1919), 272.

Even towards acids, magnesium sometimes shows "passivity."[2] For instance, the metal is attacked readily by 5 per cent. acetic acid, but the addition of 1 per cent. of potassium dichromate completely stops the reaction. On the other hand, the addition of chlorides causes the action to recommence. Here again the passivity is probably due to a closely adherent oxidized film, which in the presence of chlorides becomes ineffective as a protective layer.

It is noteworthy that amalgamated magnesium is less liable to passivity (partial or total) than pure magnesium[3]; possibly the oxide does not adhere so readily to an amalgamated surface.

Magnesium, when heated in air, burns with a very brilliant flame. The light emitted is of an intense bluish-white colour, very rich in ultra-violet rays. No doubt the brightness is due to incandescent particles of magnesium oxide. The light is quite different from that evolved by flames containing metals in the vaporous state.

Having a more negative electrode potential than any other metal which is stable towards water, magnesium is capable of precipitating many other metals from solutions of their salts. To some extent, the oxide-film interferes with this, but if the solution is even slightly acid the replacement at once occurs. Thus magnesium immersed in a solution of copper sulphate liberates metallic copper, although hydrogen is always evolved at the same time.

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[1] U. R. Evans, *Trans. Faraday Soc.* **18** (1922), 3.

[2] R. Lohnstein, *Zeitsch. Elektrochem.* **13** (1907), 613.

[3] See B. P. Beck, *Rec. Trav. Chim.* **41** (1922), 353, who has compared the electrode potentials of pure and amalgamated magnesium immersed in numerous solutions.

Laboratory Preparation. Magnesium has too negative a normal electrode potential to be deposited in the elemental condition by the electrolysis of an aqueous solution of a salt. The element can be formed by the electrolysis of fused magnesium chloride, the melting-point of which is conveniently lowered by the addition of potassium chloride.[1] The fused salts must be quite free from moisture and from magnesium oxide; any traces of oxide present can be converted to the chloride by adding a little ammonium chloride to the fused mixture. The electrolysis may be carried out in a graphite crucible, which serves as cathode, a carbon rod being introduced as an anode. Precautions must be taken that the molten magnesium formed at the cathode does not become attacked by the chlorine produced at the anode, or by atmospheric oxygen. The magnesium is deposited in a somewhat spongy condition, but can afterwards be melted up to a button under a covering of calcium fluoride.

If during electrolysis the fused mixture becomes too impoverished in magnesium, the precipitation of potassium at the cathode may commence. This can be recognized by the bath becoming blue; the presence of metallic potassium and sodium in fused salts usually causes a blue colour. The remedy is obvious. Dark spots are sometimes produced in the electrolyte during the preparation of magnesium; these have been ascribed to the formation of a suboxide; they only appear if the electrolyte employed contains traces of magnesium oxide.[2]

Compounds

Magnesium oxide, MgO, is formed, together with a small amount of nitride, when the metal is burnt in air. If the combustion takes place in oxygen, the oxide only is produced. The same substance is formed by heating the carbonate or nitrate. Several varieties exist, differing greatly in density, the strongly ignited form being less reactive than the more voluminous forms. The hydrate, **magnesium hydroxide,** $Mg(OH)_2$, is formed as a white precipitate by the addition of caustic soda or potash to a solution of a magnesium salt. It is probably a definite chemical compound. The hydroxide is only very sparingly soluble in water (about 1 part in 50,000), but the solution is distinctly alkaline to indicators. The same precipitate is formed when ammonia is added to a solution of a magnesium salt, but it is not precipitated if an ammonium salt is present, for reasons explained in Chapter VI (Vol. I).

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[1] S. A. Tucker and F. L. Jouard, *Trans. Amer. Electrochem. Soc.* **17** (1910), 249.

[2] H. C. Frary and H. C. Berman, *Trans. Amer. Electrochem. Soc.* **27** (1915), 209.

Soluble Salts. When magnesium or its hydroxide is dissolved in an acid, a solution of a magnesium salt is produced. The salts themselves can be isolated from this solution by crystallization. The **sulphate**, $MgSO_4.7H_2O$, forms colourless rhombic prisms isomorphous with the sulphates of many other divalent elements (such as zinc, cadmium, nickel and ferrous iron). The **nitrate**, $Mg(NO_3)_2.6H_2O$, and the **chloride** are deliquescent, like the corresponding beryllium salts. The chloride is not easy to obtain in the anhydrous state by the evaporation of a solution of the oxide or carbonate in hydrochloric acid. When such a solution is concentrated, one of the hydrated chlorides (usually $MgCl_2.6H_2O$) is deposited. If we attempt to drive off the water of crystallization by heating the solid hydrate, the salt is converted in part to the oxide, thus

$$MgCl_2 + H_2O = MgO + 2HCl,$$

hydrogen chloride being evolved. In the presence of air, chlorine is also produced,

$$MgCl_2 + O = MgO + Cl_2.$$

Consequently, the ultimate product of evaporation of the chloride solution consists in a large degree of oxide. However, hydrated magnesium chloride can be successfully freed from water by heating in a current of hydrogen chloride; the presence of excess of this gas, which is one of the products of the change,

$$MgCl_2 + H_2O = MgO + 2HCl,$$

prevents the decomposition from taking place. The anhydrous chloride dissolves in water with the evolution of heat.

Insoluble Salts. As in the case of beryllium, the insoluble salts include the **carbonate** and **phosphate.** When a magnesium sulphate solution is precipitated by sodium carbonate, a basic magnesium carbonate (or mixture of basic carbonate and hydroxide) is produced. A light variety is obtained when precipitation is conducted in the cold, and a denser product is obtained from a boiling solution. The carbonate, although almost insoluble in pure water, is quite soluble in water containing carbon dioxide, a soluble bicarbonate being no doubt produced, as in the case of the corresponding calcium compound.

Various phosphates of magnesium are produced by precipitating a solution of a magnesium salt with the different phosphates of sodium. The acid phosphates are comparatively soluble. When a magnesium salt solution is treated with sodium phosphate in the presence of ammonia, an insoluble double phosphate, $Mg(NH_4)PO_4.6H_2O$, is thrown down as a crystalline precipitate. This substance on heating leaves magnesium pyrophosphate, $Mg_2P_2O_7$.

$$2Mg(NH_4)PO_4 = 2NH_3 + Mg_2P_2O_7 + H_2O.$$

Magnesium nitride, Mg_3N_2. Magnesium is the first metal to be considered, which forms a nitride of sufficient importance to call for remark. It will be seen later that, in the case of several of the metals that follow, notably aluminium, titanium and vanadium, the nitrides are quite stable compounds. Magnesium nitride is formed to a small extent when magnesium is burnt in air; it is produced free from oxide when the metal is heated in a current of nitrogen, or in gaseous ammonia. It is usually described as a yellow-green substance, which gradually decomposes when exposed to damp air, ammonia and magnesium oxide (or hydroxide) being formed. The same change occurs quickly, with considerable development of heat, when the nitride is introduced into water.

Magnesium peroxide. When sodium peroxide is added to a concentrated solution of a magnesium salt, a white precipitate which contains a hydrated form of a peroxide, mixed with the ordinary hydroxide, is produced.

Organic Compounds of Magnesium. Very important compounds are formed by the action of certain organic iodides in ethereal solution upon magnesium turnings. Thus an ethereal solution of methyl iodide (CH_3I) yields the compound $CH_3.MgI$; this compound can be isolated as a solid when the ether is removed by evaporation, although the crystals obtained still contain one molecule of "ether of crystallization." Other analogous compounds, such as $C_2H_5.MgI$, are known. They are much used in organic chemistry under the name of **Grignard's reagents.**

Analytical

Salts of magnesium are characterized by no marked colour reaction, but the distinction and separation of the element from other metals is not very difficult. Since the insolubility of the hydroxide is far from complete, the metal is not precipitated by ammonia in the presence of ammonium salts. It is also not precipitated by hydrogen sulphide, nor by ammonium sulphide (for magnesium sulphide is decomposed by water); nor yet by ammonium oxalate (for magnesium oxalate is not sufficiently insoluble). Now, practically all other metals, except magnesium and the alkali-metal group, are thrown down as an insoluble compound by one or other of the reagents mentioned, and can therefore be separated. Afterwards magnesium can be separated from the alkali-metals by virtue of the insolubility of the double ammonium magnesium phosphate in solutions containing ammonia. The hot solution is made strongly ammoniacal, and sodium phosphate is added. The solution is stirred well, and allowed to stand for some time; the magnesium comes down as a crystalline precipitate consisting of the double salt, $Mg(NH_4)PO_4$. The precipitation requires time, but, if the conditions are right, it is quite complete; the precipitate can be filtered off, washed with water containing ammonia and ignited with the filter paper. The residue is weighed as magnesium pyrophosphate, $Mg_2P_2O_7$.

The common alkali metals are not precipitated under these conditions; but, if lithium should be present, its phosphate, which is also insoluble, would be thrown down at the same time. In consequence, if the mixture of salts should contain lithium, the magnesium is not directly precipitated as phosphate, but is thrown down as hydroxide by boiling with milk of lime. The precipitate consists of hydroxides of calcium and magnesium. It is dissolved in a little acid, and then made ammoniacal. The calcium is first separated as insoluble oxalate, and the magnesium afterwards precipitated as the double phosphate in the manner just described.

TERRESTRIAL OCCURRENCE

Magnesium is an element which occurs very abundantly on the earth. In the consolidation of intrusive igneous masses, the magnesium has separated for the most part in the portions that have solidified in the comparatively early stages, that is the basic and intermediate portions. Here we find crystals of such minerals as

Olivine (or peridote) . . $(Mg,Fe)SiO_4$

as well as far more complex silicates like augite and hornblende, both of which contain magnesium.

When these rocks are exposed to the action of water and carbon dioxide, they readily undergo changes. Occasionally, the magnesium remains in the mass after the alteration. Peridotite, for instance, an ultra-basic rock consisting largely of olivine, becomes weathered to serpentine-rock. The main consituent of the latter is a hydrated silicate of magnesium,

Serpentine . . . . . $3MgO.2SiO_2.2H_2O$.

formed by removal of most of the iron. The altered rock has a mottled appearance containing red portions, the colour of which is due to oxide of iron derived from the original olivine; the altered crystals of olivine are generally traversed by a regular network representing the old cracks through which the water which caused the change must have penetrated the olivine, and along the lines of these cracks remain strings of particles of magnetite (Fe_3O_4). The mesh-structure which is characteristic of serpentine is due to this cause.

It is probable that the important mineral

Talc . . . . . $3MgO.4SiO_2.H_2O$

is also produced by the alteration of ferro-magnesian silicates, although very likely from minerals like augite and hornblende, rather than from olivine.

By the action of carbon dioxide and water upon rocks rich in magnesium, the carbonate is frequently produced, and it is probable that some of the important deposits of

Magnesite . . . . $MgCO_3$,

notably those of Euboea (Greece) have been formed in this way. In such cases magnesite is usually associated with serpentine. On the other hand, the Styrian magnesite, as we shall see, has a different mode of origin.[1]

But in most cases the more important result of weathering has been to remove the magnesium in solution, and consequently all natural waters which have passed through magnesium-bearing rocks come to contain magnesium. Soluble salts of magnesium are normal constituents of river-water, and are thus carried into the sea. Where reefs of coral or deposits of shell have been formed on the bed of the ocean, and are in the process of being consolidated into limestone ($CaCO_3$), the magnesium salts often act upon the calcium carbonate, part of the calcium being replaced by magnesium, so that the mineral

Dolomite . . $CaCO_3.MgCO_3$

is formed. In such cases, the strata, instead of hardening into true limestone, comes to form " magnesian limestone " or " dolomite-rock." Sometimes as a result of further alteration the whole of the calcium may be eliminated, leaving magnesite. The important magnesite beds of Styria have been formed in this way.

It is quite likely that, in many cases, the " dolomitization " of limestone may occur long after the calcium carbonate deposit has been consolidated into hard rock, through the agency of magnesium-bearing waters permeating through the rock in question. Possibly much of the magnesian limestone of England was originally ordinary "carboniferous limestone," but has undergone alteration through percolating waters containing magnesium salts derived from the Permian and Triassic rocks above it. There has been a certain amount of disagreement among geologists, however, regarding the question of dolomitization.

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[1] For mode of origin of magnesite see F. W. Clarke's " Geochemistry " (published by U.S. Geol. Survey).

A considerable part of the magnesium which finds its way to the sea, however, is not removed, and so the metal tends to accumulate in the water. Normal sea-water contains magnesium to the extent of about 0·5 per cent. of magnesium chloride (reckoning the whole of the magnesium as chloride), but the waters of many of the bitter lakes of desert regions, which have partially evaporated, contain much more. The Dead Sea contains over 9 per cent. But it is only where inland lakes have gone through a long process of evaporation—as at Stassfurt—that the deposition of solid magnesium salts has taken place. In the upper parts of the salt beds at Stassfurt, where potassium deposits occur, magnesium is also found. Of course, the principal source of potassium,

Carnallite . . . . $KCl.MgCl_2.6H_2O$

contains magnesium, whilst other minerals found at Stassfurt, such as the sulphate,

Kieserite . . . . $MgSO_4.H_2O$,

contain magnesium as the only metal.

TECHNOLOGY AND USES.

Manufacture and Uses of Magnesium Oxide and Magnesia Refractories. The main employment of magnesium compounds is due to the high melting-point of magnesium oxide. Both calcined magnesite and calcined dolomite are used as **refractories** for the lining of furnaces, and for other purposes where a material with a high softening-temperature is required. Calcined magnesite consists essentially of magnesium oxide (MgO), although it may also contain iron oxide which considerably lowers the melting-point; calcined dolomite naturally consists of a mixture of magnesium and calcium oxides. Calcined magnesite is preferable, but more expensive, magnesite being much less common than dolomite. The employment of both substances is very extensive in the manufacture of steel by the "basic process." Here the slag, which must have a distinctly basic character, would readily interact with a furnace lining of silica (the refractory employed in the "acid steel process"). A basic lining for the hearth is therefore necessary.

Calcined magnesite is largely employed in steel-furnaces in the form of magnesite bricks. The bricks made from Styrian magnesite were formerly considered to be the best. This was not so much due to the quality of the original Styrian magnesite, as to the care with which it was selected, calcined and graded. Early attempts to prepare magnesite bricks in England—chiefly from Greek magnesite—were not very successful. The raw material found in Greece is actually purer than that found in Styria, but for this very reason it requires to be subjected to a higher temperature before sintering occurs, unless a "bonding agent" is employed. Moreover, the Greek magnesites have, as stated above, an entirely different mode of origin from the Styrian ones, and differ from the latter in structure; this may also contribute to the difference in behaviour of the two varieties on burning. With experience it has become possible to produce from Greek magnesite bricks perfectly suitable for the steel-makers, and it is hoped shortly to excel the Styrian product.[1]

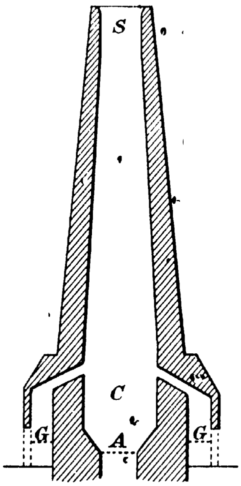

FIG. 12.—Continuous Kiln.

The calcination of the magnesite generally takes place in vertical kilns which may be either continuous or intermittent. The continuous kilns are tall (perhaps 40 feet in height) and narrow. Fig. 12 shows a kiln heated by flames from burning fuel (coal or lignite) in the grates G. The magnesite is charged in continuously at the top of the shaft (S) so as to keep the kiln full. As the magnesite descends, it becomes intensely heated by the ascending gases, and passes into the cooling-space C completely converted to magnesia (MgO). Here the charge of magnesia is cooled by the incoming air and can thus be dropped directly into trucks placed below, A, whilst the incoming air is at the same time heated, and enters the kiln proper at a high temperature.

Where the calcined magnesite is required for making refractory bricks, a very high burning temperature (1,400–1,700° C.) is to be preferred, as the sintering of the material should be aimed at. If too low a temperature is employed, the bricks are likely to shrink and crack, when they are ultimately put to use in the lining of a furnace. In the manufacture of the bricks, the calcined material obtained from the kiln is ground, partly to coarse granules, and partly to fine powder; a mixture of the coarse and fine varieties is made into a paste with water, kept for about a week, and then pressed into brick form; sometimes a little dextrin or some other substance is added as a binder. The bricks are then burnt in the same way as ordinary bricks, but at a higher temperature.

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[1] T. Crook, *Trans. Ceram. Soc.* **18** (1918), 67; W. Donald, *Trans. Ceram. Soc.* **17** (1918), 486.

In the lining of steel-furnaces, magnesite bricks are usually employed at the base, but often a plastic mixture of ground calcined magnesite and tar (or calcined dolomite and tar) is applied above the bricks, the mixture being pressed or rammed into position, so as to form a thick layer over the whole surface to be protected. When the furnace is heated, this becomes consolidated into a hard mass, and will withstand very high temperatures without serious alteration.

Dolomite bricks are made in a similar way, but do not "travel" well; they are usually made on the spot where they are to be used. The dolomite employed for lining the hearth of a basic steel-furnace is, however, mainly applied in a plastic form mixed with tar, as described above; the dolomite intended for the plastic mixture should not be too strongly ignited.

Besides its use as a refractory, calcined magnesia has a considerable employment in chemical processes. For such purposes the high temperatures of burning mentioned above are not necessary or even desirable. Intermittent kilns of comparatively primitive character still give satisfactory results in many chemical works. These are generally much shorter and broader than the continuous kilns, and there is in most cases no external grate; the fuel needed to produce the necessary heat is introduced into the kiln itself along with the charge. When the kiln is full, the fuel is lighted and burns for perhaps two or three days; the kiln is afterwards opened, and the magnesite—now changed to oxide—is removed. Clearly, since the kiln cools down after every run, the fuel consumption of intermittent working is higher than that of continuous working, and the labour-cost is also heavy. Moreover the type of kiln in which the fuel is burnt in the shaft (*short flame firing*) requires a better grade of fuel than that in which an external fire-place is provided (*long flame firing*); for in the first case, the ashes of the fuel come out mixed with the product.

When magnesium oxide is "slaked" with water, it forms magnesium hydroxide, and the suspension of the last-named substance in water (known as *milk of magnesia*) is often a convenient form of mild alkali. It is, moreover, the starting-point of one process of making potassium chlorate. (See page 83.)

Uses of Magnesium Salts. Several of the soluble salts of magnesium are derived from the bye-products of the Stassfurt potassium industry. Magnesium chloride, for instance, is left behind, after the separation of potassium chloride from a solution of carnallite. The sulphate also occurs, as kieserite, in the Stassfurt deposits, in a hydrated form. The pure sulphate, which is obtained by recrystallizing the natural product, has recently found rather extensive employment in the Grillo process of making sulphuric acid. The choice of magnesium sulphate for the purpose is not due to any chemical property that the salt possesses, but simply to the porous, feathery character of the anhydrous salt left behind when water is driven by heat from the hydrate $MgSO_4.7H_2O$. If, before the ignition, a little platinum salt be mixed with the magnesium sulphate, finely-divided platinum is left distributed throughout the porous mass. The mass constitutes a most active catalyst for causing a mixture of sulphur dioxide and oxygen to combine to form sulphur trioxide, the great activity of the catalyst being no doubt due to the large surface presented by the anhydrous sulphate. The soluble character of the salt will also be appreciated when—as will inevitably happen after a time—the platinum becomes "poisoned" through the adsorption of arsenic or other impurities contained in the gases. It is a comparatively easy matter to dissolve the whole of the magnesium sulphate in water, after which the small amount of metallic platinum can be separated by filtration and can then be purified.

Magnesium salts find employment in medicine. The sulphate is best known under the name of *Epsom salts*. The solution of the bicarbonate is also of value. Various effervescent mixtures, consisting essentially of dry magnesium carbonate and citric acid, are popular; they evolve carbon dioxide violently when stirred with water.

A mixture of magnesium chloride and oxide, usually containing other substances, is used as **Sorel cement.** When moistened with water, it sets to a marble-like mass consisting of a basic chloride. For flooring purposes, a mixture containing 40 per cent. of magnesia, 10 per cent. of magnesium chloride, along with "fillers" such as clay, sawdust, and "terra alba" and colouring matter such as Venetian Red, has been recommended.[1] The nature of the "setting" process is probably similar to that of plaster, which is considered in the section on calcium.

Manufacture of Metallic Magnesium.[2] Lastly it is necessary to deal with the manufacture of magnesium metal, which is now an important industry. The manufacture has for some time been carried on in Germany, and was developed during the war in England. On the American continent, it has been established—like most electrolytic processes—in places where cheap water-power is available, for instance at Niagara and at Shawinigan Falls (Canada), where a metal of 99·75 per cent. purity is now produced. In Germany, the magnesium salts required are obtained from Stassfurt, whilst in America, the magnesium chloride needed is either prepared by the evaporation of the water of bitter lakes, or from the natural deposits of magnesite, which occur in various districts, notably near Ottawa and in California.

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[1] R. B. Shively, *J. Ind. Eng. Chem.*, 8 (1916), 679.

[2] S. T. Allen, *Electrician*, 68 (1922), 92; J. T. Rooney, *Met. Chem. Eng.* **22** (1920), 60; *J. Soc. Chem. Ind.* **37** (1918), **114R**, **141R**; **38** (1919), **126R**; **40** (1921), **106R**, **389R**.

The process generally consists in the electrolysis of a fused mixture of magnesium chloride mixed with potassium chloride or sodium chloride to lower the melting-point. There are two serious difficulties to be faced. Firstly, in preparing anhydrous magnesium chloride by heating the hydrated chloride, hydrogen chloride is often driven off, leaving magnesium oxide, the presence of which is fatal to the success of the subsequent electrolysis. Secondly, magnesium metal is lighter than the fused mixture of salts, and will tend to float to the surface, and recombine with the chlorine evolved at the anode.

As an example of a method of overcoming these difficulties, a process recently developed at Wolverhampton, may be referred to. The process produces not only metallic magnesium but also potassium chlorate. The source of the magnesium is magnesite. The magnesite is calcined to give magnesia, which is ground and suspended in water. Into the "milk of magnesia" thus formed, chlorine gas (provided from the electrolytic cells mentioned below) is passed, magnesium chloride and magnesium chlorate being formed in solution. The liquid is concentrated, and allowed to deposit half its magnesium chloride. Afterwards the clear liquor is treated with potassium chloride; potassium chlorate, being much less soluble, crystallizes out almost quantitatively. The magnesium chloride is dehydrated by heating at 150° C. in a current of dry air, but, as this gives rise to a certain amount of oxide, the product is afterwards treated with hydrogen chloride gas at 300° C. In that way pure anhydrous magnesium chloride is obtained.

The electrolysis takes place in two stages. In the *first stage*, the cathode is a bath of molten lead, upon which floats a layer of the fused electrolyte, consisting of magnesium chloride and other chlorides. Graphite anodes dip into the electrolyte, and come to within ¾ inch of the lead cathode; 5 volts are applied to each cell, and both the molten lead and the electrolyte are circulated. At the anodes, chlorine is evolved, whilst at the cathode magnesium is produced, and dissolves in the lead; the lead-magnesium alloy, owing to its weight, remains at the bottom of the cell, and is not attacked by the chlorine. The chlorine is used for the treatment of fresh milk of magnesia. In the *second stage*, the lead-magnesium alloy is made the anode, the electrolyte being the same as before, whilst the cathodes are of steel. In this stage, magnesium is dissolved from the anode, leaving more or less pure lead, whilst pure metallic magnesium is deposited at the cathode. Since in this second stage no gaseous chlorine is evolved, there is no exceptional difficulty in obtaining a good yield of the metal.

Magnesium comes on to the market partly in "stick-form," partly as a powder. Its uses are numerous.[1] Owing to the powerful affinity of magnesium for oxygen, it is added in small quantities as a "deoxidizer" to bronze, copper, aluminium and steel in order to reduce the last trace of oxide which would otherwise cause intergranular weakness in the material.

Owing to the brightness of the light evolved when magnesium burns, and its richness in actinic rays, magnesium powder is the essential constituent of the flashlight powders used in photography. The metal is also required for military star-shells and other forms of light signal.

A good deal of magnesium is consumed for the ignition of thermite charges, and a certain amount is utilized for miscellaneous purposes in chemical industry as a reducing agent or even as a dehydrating agent.

Owing to its lightness, magnesium is a constituent of many of the light alloys which will be discussed in the section dealing with aluminium. There are also a few light alloys containing magnesium, but no aluminium. As an example, the alloy known as "electron" may be mentioned: it contains 95 per cent. of magnesium, 4·5 per cent. of zinc and 0·5 per cent. of copper, and has a specific gravity of only 1·79. It is remarkably strong—considering its lightness—and has good machining properties.[2]

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[1] W. M. Grosvenor, *Trans. Amer. Electrochem. Soc.* **29** (1916), 521.

[2] S. Beckinsale, *J. Inst. Met.* **26** (1921), 375; Hanszel, *Zeitsch. Metallkunde*, **13** (1921), 325.

CALCIUM

Atomic weight . . . 40·07

The Metal

Fresh calcium is a silver-white metal, softer than magnesium, but possessing a rather higher melting-point (800° C.). Calcium is quite volatile at its melting-point. The specific gravity is 1·55, lower than that of the previous member of the group.

Calcium is a considerably more reactive metal than magnesium, and its chemical properties are more like those of the alkali-metals. When placed in water, the element decomposes it slowly, hydrogen being evolved. The hydroxide produced is too soluble to protect the metal entirely against attack, but calcium reacts with water much less violently than sodium, for instance, which stands lower in the potential series and has also a more soluble hydroxide. If the water be weakly acidified, the evolution of hydrogen becomes far more rapid. Curiously enough calcium is scarcely attacked by concentrated nitric acid ; this remarkable fact—so much at variance with the other properties of calcium—seems to be comparable to the passivity of iron in strong nitric acid.

Although the metal is unaffected by dry air, it becomes oxidized if exposed to atmospheric moisture. When heated in air it burns with a bright flame.

Laboratory Preparation. Calcium cannot be obtained by electrolysis of an aqueous solution, but is prepared by the electrolysis of fused anhydrous calcium chloride, the melting-point of which can be lowered by the addition of calcium fluoride.[1] The calcium chloride should be perfectly free from water and calcium oxide ; it is best to mix it with a little ammonium chloride and to heat it at about 500–600° C. in order to ensure that moisture has been driven off. If the least trace of moisture remains, hydrogen will be produced, instead of calcium, on electrolysis.

It is usual to conduct the electrolysis in a graphite crucible which forms the anode, the cathode being an iron ribbon which is raised continuously as the calcium is deposited on it. The calcium adheres to the iron, and thus a stick of solid calcium is produced. It is necessary to keep the temperature as low as is consistent with the fluidity of the bath, since otherwise the calcium is liable to become oxidized. In one variation of the method, the cathode is a water-cooled metal tube.

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[1] A. R. Johnson, *J. Ind. Eng. Chem.* 2 (1910), 466. The papers by P. H. Brace, *J. Inst. Met.* 25 (1921), 153, and *Trans. Amer. Electrochem. Soc.* 37 (1920), 465, should also be consulted, although they refer to production on a slightly larger scale.

Compounds

Calcium oxide (*quicklime*), CaO, is formed when the metal is burnt in oxygen; if the combustion proceeds in air, the product contains nitride and generally carbonate.

It may be prepared by heating calcium carbonate, but, since it is a more strongly basic oxide than magnesia, the dissociation into basic and acidic oxides

$$CaCO_3 = CaO + CO_2$$

requires a much higher temperature than the analogous dissociation of magnesium carbonate. At every temperature there is a definite pressure of carbon dioxide which can be produced by the decomposition of calcium carbonate before the reaction ceases. At low temperatures, however, a very low pressure of carbon dioxide is sufficient for the equilibrium,

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

At 812° C., the pressure of carbon dioxide needed for equilibrium is equal to the pressure of the atmosphere (760 mm. of mercury). It is only above this temperature that the decomposition of calcium carbonate becomes rapid under ordinary conditions.

If calcium carbonate is heated at a temperature below 812° C., it will commence to decompose. But as soon as the partial pressure of carbon dioxide above it comes to the equilibrium value the change ceases. For the pressure will not be sufficient to drive forward the gas from the vessel in which heating is taking place, and, although a little carbon dioxide may pass out by diffusion and will then be replaced through the decomposition of fresh calcium carbonate, the rate of change due to this cause will in general be very small. But now consider what will happen if a substance like carbon is present, which reacts with, and destroys, carbon dioxide at the temperature in question. Directly the carbonate is heated with carbon, a certain amount of carbon dioxide is formed as before; but, before the pressure due to this gas reaches the equilibrium value, it will react with the carbon thus

$$CO_2 + C = 2CO,$$

carbon monoxide being produced. Thus fresh carbon dioxide will be formed by the decomposition of carbonate to replace that lost through reaction with carbon, and this in its turn will be destroyed.

The decomposition of calcium carbonate will continue indefinitely at quite moderate temperatures without the pressure of carbon dioxide ever reaching the value which would cause the decomposition to cease. It follows, therefore, that the presence of carbon enables us to carry out the decomposition of calcium carbonate at temperatures at which under other circumstances the decomposition would not take place. As a whole, the reaction of the preparation of calcium oxide from the carbonate at temperatures below 812° C. by the aid of carbon must be written

$$CaCO_3 + C = CaO + 2CO.$$

Calcium oxide is a white substance, which melts at a very high temperature (about 1,995° C.), although lower than that at which magnesia fuses. When heated, it becomes, like magnesia, incandescent. It is a distinctly basic oxide; if carbon dioxide is passed over it, the gas is absorbed, calcium carbonate being produced.

Calcium oxide has a very great affinity for water. Although it combines with less violence than the oxides of potassium and sodium, the reaction between lime and water is accompanied by a considerable evolution of heat. When exposed to damp air, quicklime takes up moisture, and becomes converted to the hydroxide. The same change occurs more readily when quicklime is made into a paste with water, the mass becoming extremely hot. The product, **calcium hydroxide** (*slaked lime*), appears to be a definite chemical compound.[1] When dried at 110° C., it has the composition $Ca(OH)_2$. It is a white substance, which is only slightly soluble in water, although more soluble than magnesium hydroxide. The saturated solution at 10°C. containing 0·3 per cent. $Ca(OH)_2$; in hot water, calcium hydroxide is even less soluble. The solution (*limewater*) is strongly alkaline, and readily takes up carbon dioxide from the air. On account of its comparatively small solubility, calcium hydroxide can be obtained by precipitation of a strong calcium chloride solution with caustic soda.

Salts. Any soluble salt of calcium may be obtained by the dissolution of the hydroxide or carbonate in the acid in question. The **nitrate** and **chloride** are deliquescent and very soluble, as in the case of magnesium. The chloride forms several hydrates; one of these, $CaCl_2.6H_2O$, is formed in transparent crystals when a solution of calcium carbonate in hydrochloric acid is concentrated by evaporation and cooled. When the crystals are heated, they lose water, the anhydrous chloride, $CaCl_2$, being finally obtained. This latter substance is a powerful dehydrating agent, readily absorbing moisture from the air, and is used for drying gases and for freeing organic liquids from the last traces of moisture. When the anhydrous chloride dissolves in water, a great deal of heat is evolved; but, on the other hand, when the hydrate ($CaCl_2.6H_2O$) is dissolved, an absorption of heat takes place. It is customary to compare the dissolution of the hydrate, which is a solid containing a large proportion of water, with the melting of ice. The parallel is not quite accurate, but it is certainly a fact worthy of notice that most hydrated salts containing large amounts of water of crystallization dissolve with the absorption of heat.

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[1] T. Selaniwanow, *Zeitsch. Anorg. Chem.* **85** (1914), 329.

Calcium sulphate, $CaSO_4$, is a much less soluble salt, and may be obtained by precipitating a strong solution of calcium chloride with sulphuric acid. Various hydrates are known, and the relations between them are discussed in the technical section.

Much more insoluble than the sulphate are the carbonate, phosphate, oxalate and fluoride of calcium. The **carbonate,** $CaCO_3$, obtained when a soluble salt is precipitated with sodium carbonate, is a light white powder. The same precipitate is formed when carbon dioxide is passed into lime-water, but dissolves again when carbon dioxide is present in excess, a clear solution of the soluble bicarbonate, $CaCO_3.H_2CO_3$, being produced.

The **phosphate,** $Ca_3(PO_4)_2$, is obtained as a white precipitate when ordinary sodium phosphate (Na_2HPO_4) is added to an ammoniacal solution of a calcium salt; if, instead of ammonia, a trace of acetic acid is present, the acid salt, $CaHPO_4$, corresponding to the sodium compound, is thrown down. Both these precipitates are soluble in dilute mineral acids, and also in phosphoric acid. From the solution in acid, a soluble phosphate, $CaH_4(PO_4)_2$, can be obtained by crystallization. The **oxalate,** CaC_2O_4, is a crystalline white precipitate, obtained by adding ammonium oxalate to an ammoniacal solution of a calcium salt; it is soluble in hydrochloric acid, but not in acetic acid. The **fluoride** is similarly formed by the interaction of sodium fluoride and calcium chloride.

Calcium Sulphides. When hydrogen sulphide gas is passed into milk of lime, and the solution produced evaporated, calcium **hydrosulphide,** $CaS.H_2S.6H_2O$, is obtained in colourless prisms. When heated it evolves hydrogen sulphide, and yields the normal **sulphide,** CaS, which is a yellow-white mass (probably quite white when pure). The sulphide is decomposed by water, giving calcium hydroxide and the hydrosulphide. The normal sulphide can be obtained in a dry way by heating the oxide with sulphur, or (in a less pure condition) by heating the sulphate with carbon.

Many samples of calcium sulphide have the peculiar property of **phosphorescence**; if exposed to sunshine the sulphide absorbs light-energy, and has the power of emitting light afterwards in the dark. This property is always connected with the presence of some heavy metal impurity. Pure calcium sulphide obtained by heating the purest lime with the purest sulphur is practically non-phosphorescent. The conditions under which it becomes phosphorescent have been the subject of lengthy researches.[1] In order to obtain a strongly phosphorescent product, there should be present, firstly, a trace of a *compound of a heavy metal*, such as copper, manganese, or bismuth, and secondly a *fluxing material*, such as a borate, phosphate, fluoride, sulphate or chloride. Without the fluxing material, it is difficult to obtain a strongly phosphorescent product, probably because calcium sulphide is nearly infusible and does not therefore dissolve the heavy metal compound when heated with it at a moderate temperature. If, however, lime and sulphur are heated with a little sodium sulphate and a trace of copper oxide (8 parts per 100,000 parts of lime), sintering takes place, and the product, after exposure to the sunlight, gives a brilliant green phosphorescence. The colour of the light emitted by the product after exposure to sunlight varies with the heavy metal present; if analysed by means of the spectroscope, it will be found to consist of definite bands, which are characteristic of the heavy metal in the material. Thus whilst copper produces in calcium sulphide a green or blue phosphorescence, nickel produces a red phosphorescence. The relative intensity of the different bands, and their persistence (i.e. the time during which the light continues to be given out) are affected by the nature of the fluxing material employed, which is consequently not without influence on the colour of the phosphorescent light. Thus calcium sulphide containing a trace of copper gives a green light if sodium sulphate is the fluxing material, but a blue light if potassium sulphate is used. It may be mentioned at this point that the sulphides of other metals of this group are also phosphorescent in the presence of heavy metals. The colour of the phosphorescent light varies considerably in the different cases. Thus the presence of copper in calcium sulphide produces a bluish-green phosphorescence, whilst in strontium sulphide it gives a yellow-green phosphorescence, and in barium sulphide an orange-red phosphorescence, borax being used as fluxing agent in each case. Magnesium sulphide shows phosphorescence in the presence of certain impurities, for instance, manganese, bismuth, or arsenic[2]; but the presence of certain other impurities, notably iron, appears to prevent phosphorescence and it is only by observing special precautions to exclude such impurities that a phosphorescent product can be obtained. The sulphide of zinc has recently been prepared in a state sufficiently pure as to be practically free from phosphorescence, but it becomes strongly phosphorescent if heated with the merest trace of a copper or manganese salt in the presence of chlorides, which act as the fluxing agents.[1]

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[1] P. Lenard and V. Klatt, *Ann. Phys.* **38** (1889), 90; **15** (1904), 225, 425, 633. See also G. Urbain, "Introduction à l'étude de la Spectrochimie" (Hermann).

[2] E. Tiede and F. Richter, *Ber.* **55** (1922), 69; *Zeitsch. Elektrochem.* **28** (1922), 20.

At least one yellow **polysulphide** of calcium exists. The pentasulphide (CaS_5) is formed when calcium sulphide and sulphur are heated in the presence of water. The same compound is produced when milk of lime is boiled with excess of sulphur, calcium thiosulphate (CaS_2O_3) being formed at the same time. Other polysulphides, notably CaS_2, have been described, but their existence is more doubtful.[2]

Calcium nitride.[3] When calcium is heated in a current of nitrogen, it often combines with the gas forming the nitride Ca_3N_2. Any sample of calcium takes up nitrogen above the melting-point, but only certain forms absorb it readily in the solid condition. For instance, coarsely crystalline calcium (obtained by the slow cooling of the molten metal) is highly active, and absorbs nitrogen between 300° and 600° C., whilst calcium obtained by quenching from 840° C. (i.e. from just above the melting-point) is said to be almost unchanged by the gas at low temperatures. The rate of reaction is not greatly increased by breaking up the metal into powder, and the combination does not seem to be essentially a surface action. It appears rather to depend on the penetration of nitrogen through the metal, for the pieces of nitride produced in general retain the form of the pieces of calcium metal employed. Calcium nitride is a brown solid, which is decomposed by water or steam, ammonia being produced.

Calcium hydride is likewise formed when calcium is heated in hydrogen. Here again different varieties of calcium show great difference in activity, and there is consequently an apparent lack of agreement between the results of different experimenters[4]; some varieties take up the gas at ordinary temperatures. The hydride forms transparent crystals of the composition CaH_2. If heated in air, the hydride burns, and when introduced into water it evolves hydrogen, calcium hydroxide being formed. It is a powerful reducing agent.

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[1] R. Tomaschek, *Ann. Phys.* **65** (1921), 189.

[2] S. J. M. Auld, *Trans. Chem. Soc.* **107** (1915), 480.

[3] A. Sieverts, *Zeitsch. Elektrochem.* **22** (1916), 15.

[4] Compare, for instance, the statement of F. Ephraim and E. Michel, *Helv. Chim. Acta*, **4** (1921), 900, with those of A. Sieverts, *Zeitsch. Elektrochem.* **22** (1916), 15.

Calcium peroxide is formed when hydrogen peroxide is added to limewater, separating from the solution in colourless crystals, of the composition $CaO_2.8H_2O$. It is a strong oxidizer, and readily evolves oxygen, becoming converted to calcium hydroxide.

Although the compound $CaO_2.8H_2O$ is colourless, it can be made to yield a yellow product when warmed with hydrogen peroxide, and this yellow product appears to contain some more highly oxidized body, possibly CaO_4.[1] The latter compound, however, has not been isolated in a pure state.

"Bleaching Powder." When chlorine is passed over perfectly dry slaked lime, no action takes place. But, if the lime contains a slight excess of water, absorption of chlorine occurs, a compound known as bleaching powder being formed. Bleaching powder evolves chlorine gas when treated with strong acids, but the solution evolves oxygen in the presence of a suitable catalyst, such as cobalt hydroxide.

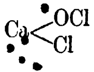
Now the interaction of chlorine and sodium hydroxide is known to give rise to a mixture of chloride and hypochlorite, thus

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

It might be expected, therefore, that a similar change would occur when chlorine is passed over calcium hydroxide,

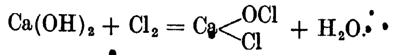
$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O.$$

According to such a view "bleaching powder" should be a mixture of chloride and hypochlorite. But, in actual fact, it is found to possess none of the properties of calcium chloride in the solid state. It is not deliquescent, and, although calcium chloride is readily soluble in alcohol, the latter liquid has practically no solvent action upon bleaching powder. In consequence, it has been suggested (originally by Odling) that bleaching powder is really a double salt, a chloride-hypochlorite of calcium, suitably expressed



$$\mathrm{Ca}<\begin{matrix}\mathrm{OCl}\\ \mathrm{Cl}\end{matrix}$$

in which case the formation can be written in the simple form



$$Ca(OH)_2 + Cl_2 = \mathrm{Ca}<\begin{matrix}\mathrm{OCl}\\ \mathrm{Cl}\end{matrix} + H_2O.$$

Odling's suggestion as to the nature of the essential constituent of bleaching powder appears on the whole to be reasonable, and most of the other views advanced on the subject seem open to objection.[1] It is probable, however, that the chloride-hypochlorite $\mathrm{Ca}{<}^{\mathrm{OCl}}_{\mathrm{Cl}}$ is hydrated; perhaps the compound

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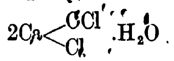
[1] W. Traube and W. Schulze, *Ber.* 54 (1921), 1626.



$$2\mathrm{Ca}{<}^{\mathrm{OCl}}_{\mathrm{Cl}}.\mathrm{H_2O}.$$

forms the main component. When bleaching powder is dissolved in water, the solution behaves as though it were a mixture of calcium hypochlorite and calcium chloride. Unchanged lime, however, exists in all samples of bleaching powder; very likely the chlorine does not get access to the centres of the grains of slaked lime, the compound formed on the outside protecting the material within from further action. For this reason bleaching powder does not form a clear solution, and the turbid liquid has a strongly alkaline reaction.

When the solution is weakly acidified, hypochlorous acid (HClO) is liberated, being a weak acid. This substance is a powerful oxidizing agent, and readily furnishes oxygen to oxidizable bodies,

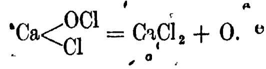
$$\mathrm{HClO} = \mathrm{HCl} + \mathrm{O}.$$

As a result the acidified solution has a bleaching action upon organic colouring matters, for the nascent oxygen attacks the dyestuffs, converting them to colourless substances. Even without the addition of acid, solutions of bleaching powder have a slow bleaching action, since a certain amount of hypochlorous acid is always present, owing to hydrolysis.

When concentrated acid is allowed to act upon bleaching powder, chlorine is evolved as a gas

$$\mathrm{HOCl} + \mathrm{HCl} = \mathrm{H_2O} + \mathrm{Cl_2}.$$

Under other conditions, bleaching powder can be made to evolve oxygen. A convenient method of preparing oxygen gas in the laboratory is to drop a little cobalt chloride solution on to bleaching powder. The free lime present in the latter liberates cobalt hydroxide, which catalytically aids the production of oxygen



$$\mathrm{Ca}{<}^{\mathrm{OCl}}_{\mathrm{Cl}} = \mathrm{CaCl_2} + \mathrm{O}.$$

Analytical

The comparatively volatile compounds of calcium impart a red colour to a Bunsen flame; non-volatile salts show the same effect if moistened with hydrochloric acid, calcium chloride being volatile at the temperature in question. The spectrum of such a flame consists of a large number of lines, mostly red, yellow, and green; there is also one line in the violet, but it is difficult to see.

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[1] G. Lunge and R. Schoch, *Ber.* 20 (1887), 1474.

Aqueous solutions of calcium salts are not precipitated by hydrogen sulphide, either in acid or ammoniacal solution, nor by ammonia in presence of ammonium chloride. In this respect calcium is distinguished and separated from the heavy metals. On the other hand, calcium is precipitated from an ammoniacal solution as oxalate by means of ammonium oxalate, differing in that respect from magnesium and the alkali metals. Two other metals of this group, strontium and barium, are thrown down with calcium as oxalate, and the separation of these three very similar elements is somewhat difficult. Probably the best method of separating strontium and barium from calcium depends on the fact that the nitrates of the two last-named metals are practically insoluble in a mixture of alcohol and ether, whereas calcium nitrate is dissolved by such a liquid.[1]

Other methods for freeing calcium from the two other metals are also based upon the difference in solubility of the nitrates. Strontium and barium nitrates are practically insoluble in concentrated nitric acid,[2] or in boiling amyl alcohol,[3] while nitrate of calcium can be dissolved by either of these liquids.

Having obtained a solution of calcium free from other metals, it is possible to precipitate the element as oxalate by the addition of ammonium oxalate to a solution containing excess of ammonia. The precipitate is washed with dilute ammonia solution, and dried. It can be heated gently and so converted to carbonate, in which form it is weighed. Alternatively, it can be ignited strongly, and weighed as oxide. In the first case, it is difficult to prevent a slight conversion of carbonate to oxide; in the second, it is troublesome to bring about a complete conversion. For this reason, the washed oxalate precipitate is frequently not weighed at all, but is redissolved in sulphuric acid, and the amount of oxalic acid liberated is determined volumetrically by titration with permanganate.

If a gravimetric method is required, it is preferable to estimate the calcium as sulphate, which is practically insoluble in a solution containing much alcohol, although quite perceptibly soluble in water. Sulphuric acid is added to the solution, if not already present, and then three or four volumes of alcohol; after standing for twelve hours, the precipitate can be filtered off, washed with alcohol, dried, ignited and weighed as calcium sulphate.

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[1] Sir W. Crookes, "Select Methods in Chemical Analysis" (Longmans), 1905 Edition, p. 45.

[2] F. P. Treadwell, "Analytical Chemistry"; translation by W. T. Hall (Chapman & Hall), 1913 Edition, Vol. I, p. 441.

[3] P. E. Browning, *Amer. J. Sci.* **43** (1892), 50, 314.

TERRESTRIAL OCCURRENCE

Calcium occurs in very large quantities in almost all intrusive igneous rocks, being most plentiful in rocks of "intermediate" composition. The complex silicate

Plagioclase felspar . . $n\text{NaAlSi}_3\text{O}_8 + m\text{CaAl}_2\text{Si}_2\text{O}_8$

as well as augite, hornblende and innumerable other silicate-minerals, contain calcium as an important constituent.

By the weathering and dissolution of such rocks, calcium comes to be a constituent of practically all running water. The "hardness" of ordinary river-water is mainly due to the dissolved salts of calcium.

By means of the rivers, calcium finds its way to the sea, but is largely taken up to form the hard parts of such marine creatures as coral, foraminifera, crinoids, and various shell-fish. The essential constituent of sea-shell is calcium carbonate, which occurs in two separate crystalline forms, the hexagonal "calcite" and the rhombic "aragonite."

By the consolidation of such remains formed in past geological ages, beds of

Limestone . . . . CaCO_3

have been produced. Limestone varies very much in character, according to its purity and past history; the white chalk of the South Downs, for instance, is very different in appearance from the black limestone of Flintshire. Of special interest are the "oolitic" limestones of Jurassic age, made up of innumerable rounded grains adhering together, like the roe of a fish; this structure is supposed to be due to the action of currents in the sea in which the calcareous deposits were laid down; the currents broke up the shells, or coral, into small fragments, each fragment forming the nucleus of a grain.

The formation of limestone is still going on; probably the ooze now being produced at the bottom of the Atlantic Ocean (consisting largely of minute foraminiferal shells) will one day harden to a limestone.

Most limestones have undergone many changes since the day when they were formed. Water containing carbon dioxide has dissolved the calcium carbonate at some points, and deposited it at others where the conditions were favourable. Thus all limestones have become more or less recrystallized. The older limestones have also undergone many alterations owing to earth-movements, and, where igneous intrusions have passed near a limestone, the rock has usually been completely recrystallized by the heat. Where the original limestone was a pure one, the only action of the heat has been a conversion to crystalline limestone, or "marble." But where the original limestone contained impurities, new minerals such as the calcium silicate,

Wollastonite . . . $CaSiO_3$

are generally found in the altered rock.

Where waters containing magnesium salts have passed through a layer of calcium carbonate, either during or after the time of its consolidation into limestone, the calcium is partly replaced by magnesium, forming

Dolomite . . . . $CaCO_3.MgCO_3$,

or even, in extreme cases, as in Styria,

Magnesite . . . . $MgCO_3$.

These changes have already been referred to. Where waters containing iron penetrate a similar bed, iron replaces the calcium, forming beds of ironstone, which contain the iron carbonate

Siderite . . . . $FeCO_3$

as well as (or instead of) calcium carbonate. Usually, through later changes, the ferrous carbonate is largely oxidized to ferric oxide or hydroxide.

On account of the removal of calcium from solution to form shells and coral, there is comparatively little accumulation of the metal in sea-water. Nevertheless, where evaporation of the sea has taken place, deposits of calcium sulphate occur in the salt-beds produced. Both

Gypsum . . . . $CaSO_4.2H_2O$

and

Anhydrite . . . . $CaSO_4$

are found in the salt-beds of Stassfurt. Gypsum is also found in the Triassic deposits of the English Midlands.

There are several other calcium minerals which are of importance. The fluoride

Fluorspar . . . . CaF_2

occurs as fine cubic crystals in veins and pockets in limestone. It has evidently been deposited through the action of waters (or perhaps vapours) containing fluorides, which have ascended from the interior of the earth; as the same waters often carry lead and zinc in solution, it is frequently associated with the ores of these metals. The crystals are often coloured blue (*Blue John*), and sometimes red. The blue colour is believed to be due to bituminous matter, but the red—at least in some cases—is caused by traces of a rare-earth compound.[1]

In addition, various phosphate materials containing calcium occur in large quantities; some of them, like

Apatite . . . $CaF_2.3Ca_3(PO_4)_2$,

are of mineral origin, whilst others, e.g. coprolite, are derived from animal remains. Deposits consisting mainly of calcium phosphate with a certain amount of carbonate occur in Florida, Algeria, Tunis, and in the Pacific Islands[2]; these are of great economic importance in the manufacture of fertilizers, but their importance lies, of course, in their phosphorus-content, not in their calcium-content.

TECHNOLOGY AND USES

Limestone is the raw material from which are derived most of the important substances containing calcium. But, quite apart from this, it has itself a great technical value. Many kinds of limestone have considerable importance as building materials. Less compact varieties are useful in metallurgy for adding to the furnace charge, either in order to make the slag more fusible (as in the smelting of a highly siliceous ore), or where a slag of a distinctly basic character is demanded by the requirements of the process (as in the basic steel process). Limestone is likewise employed in glass-making, being the usual form in which calcium is added to the glass mixture.

Quicklime (CaO) is produced by burning limestone in kilns by processes[3] similar to those described in connection with the burning of magnesite. Both *continuous* and *intermittent* kilns are used, the former being naturally more economical of fuel. As in the burning of magnesite, it is possible to classify the kilns into *long-flame* kilns provided with an external grate, and *short-flame* kilns in which the fuel is introduced along with the limestone into the shaft; in the second type the lime is contaminated with the ashes. Coal, coke, wood and producer-gas are all employed as fuels in different places.

The decomposition of limestone proceeds less readily than that of magnesite. As pointed out in the theoretical section, the decomposition of calcium carbonate in the presence of carbon dioxide at atmospheric pressure only takes place above 812° C. In most modern kilns, the temperature obtained exceeds that value; a temperature of 1,200° C. is often reached in the "short-flame" type of kiln. It should, however, be remembered that owing to the draught in the kiln, the partial pressure of carbon dioxide will generally be far below 760 mm., and the decomposition may proceed, therefore, even where the temperature is below 812° C., the carbon dioxide being carried off as quickly as it is formed.

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[1] C. G. Garnett, *Trans. Chem. Soc.* **117** (1920), 620.

[2] W. Packard, *J. Soc. Chem. Ind.* **40** (1921), 288R.

[3] See E. B. Dancaster, "Limes and Cements" (Crosby Lockwood); B. Block, "Das Kalkbrennen im Schachtofen mit Mischfeuerung" (Spamer).

The quality of lime depends largely on the limestone from which it is made. If the limestone is impure, a lime is produced which is said to be *lean*, since it will not combine with water so easily as a pure or *fat* lime. The best lime is "amorphous" in appearance, and combines readily and completely with water, crumbling to powder and forming *slaked lime* or calcium hydroxide. But if the lime has been heated too strongly, it may become semi-fused, and forms a compact substance which only reacts with water very slowly; such lime is said to be *dead-burnt*. This undesirable condition is produced in pure lime only at very high temperatures, such as are never obtained in a lime-kiln; but in the presence of impurities, such as silica or alumina, the softening-point is considerably reduced. Limestone containing clayey material (aluminium silicate) gives a lime (*Hydraulic Lime*) which "slakes" only with difficulty, but which when mixed with water, sets in a few days to a hard mass. It can be regarded as a variety of cement and is quite useful in mortar and cement mixtures.

On the other hand, extremely pure lime is required for chemical purposes, and especially for the manufacture of bleaching powder. A very pure lime derived from the limestone of Buxton (Derbyshire) is employed considerably by the chemical manufacturers of Lancashire and Cheshire.

The reaction between lime and water causes the evolution of a great deal of heat, and fires have arisen through the access of water to places where quicklime is stored.

Although much of the quicklime produced is converted into slaked lime by hydration with water, it is used for certain purposes in the anhydrous condition. It is still employed in lining furnaces, although for this purpose calcined dolomite or magnesite is more suitable. It is also used as one of the raw materials in the manufacture of calcium carbide.

Slaked lime is obtained by the action of water on quicklime, which is usually spread over a floor to the depth of a foot, and sprinkled with water from a hose. Much heat is evolved, and the mass at first swells up, but finally subsides again. Towards the end of the process the material should be mixed up, so as to ensure uniformity of composition.

Slaked lime is the cheapest alkaline hydroxide known. It is used, for this reason, in numerous chemical operations. In the Solvay soda-process, for instance, lime is employed to liberate ammonia from the ammonium chloride which remains after the precipitation of sodium bicarbonate. Slaked lime is moreover used in making sodium hydroxide from sodium carbonate. In numerous chemical and metallurgical processes, aqueous solutions of salts are freed from iron, a most common impurity, by the action of lime, the iron being precipitated as the insoluble ferric hydroxide. It is also used to absorb noxious acidic substances from gas-mixtures. The dilute sulphur dioxide formed by roasting sulphide ores (especially zinc-blende)—which is often too dilute for conversion into sulphuric acid, and yet too strong for discharge into the air—may be absorbed in "milk of lime," calcium bisulphite being the product. Coal-gas is also freed from certain impurities, chiefly carbon dioxide, and to a lesser extent hydrogen sulphide and carbon disulphide, by means of lime. Many organic acids are isolated as the calcium salts; thus lime is used to absorb the vapours of acetic acid in the manufacture of that substance; again, in the preparation of oxalic acid by the oxidation of sugar or cellulose, it is precipitated as insoluble calcium oxalate by the addition of lime. Lime is furthermore used in water-softening, to convert the soluble calcium bicarbonate to the insoluble carbonate.

In most of these cases the slaked lime, being somewhat insoluble, is added as the suspension in water, known as *milk of lime*.

Apart from the examples just given, a large quantity of specially pure slaked lime is used in the manufacture of bleaching powder. Much of the chlorine obtained from the electrolytic alkali-works is absorbed in dry slaked lime with the production of that substance. A little is also absorbed in hot milk of lime, in which case calcium chlorate is obtained; this is actually the first step in one process of making potassium chlorate.

Manufacture and Uses of Metallic Calcium.[1] Metallic calcium is now produced industrially, in more than one country, by the electrolysis of fused calcium chloride. Calcium fluoride or other salts are sometimes added to reduce the melting-point, but it is stated that the best results are obtained with pure calcium chloride. The essential condition for success is that the salt must be perfectly anhydrous; it is usually heated with ammonium chloride before use; one authority recommends treatment of the fused salt with a little metallic calcium before electrolysis is begun.

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[1] P. H. Brace, *Trans. Amer. Electrochem. Soc.* **37** (1920), 465; *J. Inst. Met.* **25** (1921), 153.

Electrolysis is usually carried out in a graphite pot (Fig. 13). Sometimes the bottom is water-cooled, which allows a crust of solid calcium chloride to form at the bottom and round the walls, thus minimizing corrosion. The anodes, A, are vertical graphite plates immersed in the fused calcium chloride. The metallic cathode is hollow and water-cooled internally, and is connected to a mechanism—electrically driven—which allows the cathode to be slowly raised during the electrolysis. At the commencement of the run, the cathode is in contact with the surface of the fused bath. The metallic calcium produced on the cathode by the electric current quickly solidifies owing to the local cooling, and as the calcium is deposited, the cathode is slowly raised at such a rate that a continuous stick of solid calcium is built up, the bottom of the stick being always just in contact with the fused bath.

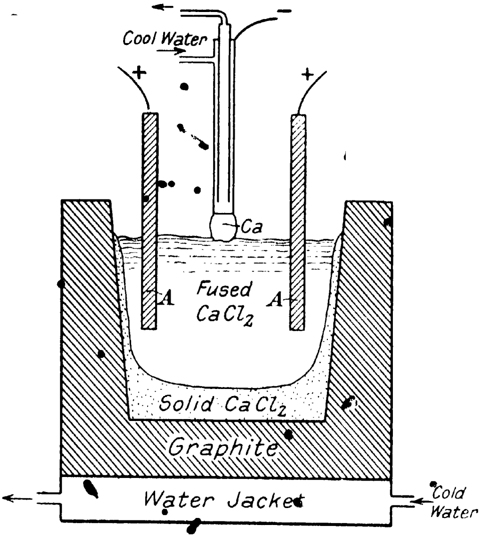

FIG. 13.—Electrolytic Production of Calcium.

Owing to its great affinity for oxygen and sulphur, calcium is sometimes added in small quantities to various metals and alloys before casting, to remove the last traces of these objectionable elements. In addition it is sometimes added to lead as a "hardener." Owing to the avidity with which calcium reacts with moisture, it is used as a dehydrating agent in organic chemistry, and it has been recommended for use in telescope tubes, to prevent the condensation of moisture on the lenses.

Manufacture of Bleaching Powder (*Chloride of Lime*). The reaction between chlorine and lime to form bleaching powder is a very simple one, but several difficulties have to be faced when it is carried out on an industrial scale. A great deal of heat is developed during the reaction, and if concentrated chlorine gas were allowed to act upon fresh lime in a confined space, the temperature would rise so high that chlorates would be formed. The poisonous nature of the chlorine introduces further difficulties, and the old "chamber process," in which workmen were sent into a chamber to shovel out the bleaching powder which lay upon the floor, must be strongly condemned. At the same time, the replacement of such a crude and unhealthy method, by the modern mechanical process which delivers the bleaching powder automatically into drums, has not been easy, because the corrosive nature of the chlorine tends to destroy the metallic portions of the moving parts of the absorption plant, and thus renewals of an expensive character may frequently be necessary. However, the plant shown in Fig. 14, whilst not entirely free from these defects, has given considerable satisfaction.

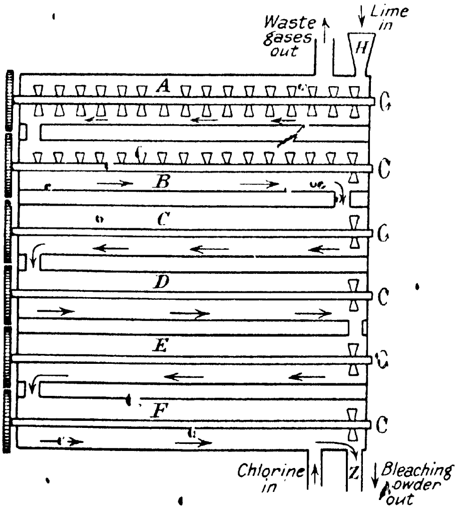

FIG. 14.—Bleaching Powder Plant.

The plant consists of a number of horizontal cylinders, each containing a rotating shaft fitted with blades, which serve to stir up the powder lying on the bottom of the cylinder and at the same time to work it along from one end to the other. The lime enters the top cylinder A through the hopper H, and is worked along the cylinder until at the end it falls into the cylinder B below; it is then worked along the length of B until it falls into the next cylinder C, and thus passes through the series, until it finally falls out through Z directly into casks, being by this time completely converted to bleaching powder. The chlorine which brings about this conversion passes in at the lowest cylinder, F, and traverses the series of cylinders in the opposite direction to the lime. In this way, the concentrated chlorine meets with lime almost completely converted to bleaching powder, and serves to complete the conversion, whilst the weakened chlorine which reaches the upper cylinders passes over fresh lime, which is an active absorbent and reduces to a minimum the amount of chlorine in the gases emerging from the top cylinder (A).

This system by which the two substances which have to react are sent through the apparatus in opposite directions is often known as the *counter-current principle* and is of very general application in manufacturing chemistry.

Strength of Bleaching Powder. If bleaching powder consisted of pure $\mathrm{Ca}{<}^{\mathrm{OCl}}_{\mathrm{Cl}}$ the whole of the chlorine would be evolved when treated with acids, and thus the content of "available chlorine" would be 55·9 per cent. If it consisted entirely of the hemihydrate $2\mathrm{Ca}{<}^{\mathrm{OCl}}_{\mathrm{Cl}}\cdot\mathrm{H_2O}$, the content would be 52·3 per cent. But since bleaching powder always contains free lime, free moisture, and traces of calcium carbonate, chloride and chlorate, the content of available chlorine always falls below this number. Thus an exceptionally good sample prepared in Lunge's laboratory contained 43 per cent., while a commercial bleaching powder is considered satisfactory if it contains 35 per cent. to 37 per cent.; the amount of non-available chlorine present as chloride and chlorate is usually between 1 per cent. and 3 per cent.

Bleaching powder keeps fairly well in temperate climates, if stored in metal cans; it decomposes very quickly if exposed to moisture and carbon dioxide, the rate of decomposition being greatly increased by sunlight. A "36 per cent. bleaching powder" will fall to about 28 per cent. in a year under favourable conditions; it will lose its strength far more quickly if it is improperly packed. In warm climates, moreover, the decomposition is always much greater; in Egypt, "11 per cent. bleaching powder" is still regarded as a good quality.[1] Even in this country, bleaching powder, when bought in small quantities, often shows a very poor content of available chlorine; this is due to inappropriate packing. Bleaching powder is rendered more stable by the addition of free lime, but for this very reason it is rendered less effective as an oxidizing agent.

Bleaching powder is still used in bleaching, although less universally than was at one time the case. One objection to it is that the solution is not clear, but contains suspended lime or calcium carbonate; sodium hypochlorite is now often employed in its place, The bleaching of wood-pulp is commonly carried out in an acidified solution of bleaching powder, although the bleaching of cotton is conducted in a distinctly alkaline bath.

Chloride of lime is largely employed as a disinfectant, and in the sterilization of water-supplies, especially in America. The presence in water of a quantity of available chlorine less than one part in a million acts as a safeguard against the presence of harmful living bacteria; the addition of chlorine to water will not prove in any way objectionable or harmful so long as the proper quantity is not unduly exceeded. It seems probable that the really active constituent is hypochlorous acid (HOCl), which is present to a small extent in ordinary solutions of bleaching powder, owing to hydrolysis, but which is only liberated in large quantities on acidification. In disinfection and sterilization, it is customary to rely upon the accidental presence of carbon dioxide to liberate the hypochlorous acid. Bleaching powder having a marked alkaline reaction is sometimes added, with the intention of sterilization, to waters which are already appreciably alkaline; such a practice appears somewhat unsatisfactory.[2]

Another use of bleaching powder is in the process of rendering wool unshrinkable. The wool is first steeped in a bath of dilute hydrochloric acid, and then in a bath containing bleaching powder; it is finally treated with a sodium bisulphite solution, to destroy the residual chlorine. The concentration of the first two baths requires careful control, since, if it is too high, the fibres become damaged. It is stated that much less damage would be caused if boric acid were used in the place of hydrochloric.[3]

Bleach-liquor is formed by passing chlorine gas through or over cold milk of lime. It consists of a mixture of calcium hypochlorite and chloride, with some free lime, and has therefore the composition of a cloudy solution of bleaching powder. It is, of course, less suited for transport than the solid material.

[1] T. Rettie, J. L. Smith and J. Ritchie, *J. Soc. Chem. Ind.* **37** (1918), 311T.
[2] See E. K. Rideal and U. R. Evans, *J. Soc. Chem. Ind.* **40** (1921), 64R.
[3] S. R. Trotman, *J. Soc. Chem. Ind.* **41** (1922), 219T.

Superphosphate. Another important calcium compound is the soluble acid phosphate known as "superphosphate of lime." As is well known, plants require phosphates for their growth. Whenever plants (e.g. grass) are consumed as food by animals, phosphates are removed from the soil. Since, therefore, the soil is continually being impoverished in these salts, it is necessary to renew the supply from without. Calcium phosphate, which forms the ash of the bones of animals, and occurs in deposits of animal origin such as guano and coprolite, would appear to be the most obvious material in which to return the phosphorus to the soil. Unfortunately, this form of phosphate is practically insoluble in water, and cannot be taken up quickly by plants. The same applies to the phosphate-fluoride mineral, apatite, and most other naturally occurring forms of phosphate. No doubt by the continued action of water, atmospheric oxygen and carbon dioxide, the minerals would be converted into some soluble phosphate, for it was in this way that phosphates originally came to exist in the soil; but such a process is too slow for modern agricultural requirements. A need, therefore, exists for the conversion of calcium phosphate into some rather more soluble form of phosphate.

Now just as calcium carbonate ($CaCO_3$) is insoluble and calcium hydrogen carbonate ($CaH_2(CO_3)_2$) soluble, so, whilst normal calcium phosphate [$Ca_3(PO_4)_2$] is insoluble, there exists a calcium hydrogen phosphate, $CaH_4(PO_4)_2$, which is dissolved comparatively readily. The method of preparing this acid phosphate is very simple. The phosphate mineral, containing normal calcium phosphate—or possibly a basic phosphate[1]—is treated with fairly concentrated sulphuric acid (specific gravity, 1·6), when some such reaction as

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

will occur. The mixture of soluble phosphate and calcium sulphate constitutes commercial "superphosphate."

The raw material, whether it consists of bone-ash, coprolites, or —as is frequently the case—phosphate rock from Florida or North Africa, must be ground to fine powder between rollers or in a ball-mill. The powder is then mixed up with acid into a paste, which is discharged into a "den," or brick chamber, designed to prevent the undue escape of heat. Here it remains for 24–36 hours, the temperature rising considerably (probably to 100° C. or even higher), as a result of the reaction. Any carbonates or fluorides in the raw materials are decomposed, carbon dioxide and hydrogen fluoride being evolved in bubbles; silicon fluoride also is often found in the gases evolved. Finally the whole mass stiffens, possibly because calcium sulphate absorbs water, being converted to the hydrated sulphate ($CaSO_4.2H_2O$). When this stiffening has occurred, the material is taken out and dried. Good superphosphate is highly porous, and no doubt much of its value is due to the large surface which it presents to the solvent action of the water in the soil.

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[1] According to H. Bassett, *Trans. Chem. Soc.* **111** (1917), 620, the phosphate contained in bone-ash, coprolites, phosphorites, etc., is not $Ca_3(PO_4)_2$, but probably $3Ca_3(PO_4)_2.Ca(OH)_2$.

At some superphosphate works, where a raw material rich in fluorine is used, the gases evolved are employed in the manufacture of fluorine compounds.

Another form in which phosphorus is added to the soil is the so-called **Basic slag** from the steel-works, which may be regarded essentially as a mixture of silicate and phosphate of calcium, although several other metals (iron, magnesium, aluminium and manganese) are present. If the slag is ground very finely in a ball-mill, it can be added to the soil without further treatment and forms a valuable source of phosphorus. It is dissolved by water more slowly than superphosphate. A very large quantity of basic slag is produced in European steel-works, especially those of Germany, where most of the iron-ores contain phosphorus; this phosphorus must be completely eliminated in the slag if the steel produced from such an ore is to be reliable. It is customary in Germany to value the slag according to the amount of phosphate soluble in citric acid. This method of estimating the value has, however, come to be discredited in this country.[1] Much of the basic slag coming from English steel-works has very little phosphate soluble in citric acid, and yet experiments have shown that this slag, if finely ground, is extremely beneficial to the soil. It is probable, therefore, that the citric acid test is of little use, and that the total phosphate content of the slag gives a better idea of the value as a manure. The cause of the comparatively low solubility of English slags in citric acid is due to the presence of fluorine. Fluorspar is commonly used at English steel-works, and the slag produced contains the phosphorus in the form of crystals of apatite, $CaF_2.3Ca_3(PO_4)_2$, a rather stable compound only slowly attacked by citric acid.[2] On account of its stability, apatite is rather slowly decomposed when placed upon the soil, and consequently the slag is actually slightly inferior as a fertilizer to the fluorine-free variety, but nevertheless gives quite good results if time is allowed.[3]

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[1] D. A. Gilchrist and H. Louis, *J. Soc. Chem. Ind.* **36** (1917), 261; G. S. Robertson, *Trans. Faraday Soc.* **16** (1921), 291.

[2] See F. Bainbridge, *Trans. Faraday Soc.* **16** (1921), 302.

[3] E. J. Russell, *Trans. Faraday Soc.* **16** (1921), 262.

During the war, practically the whole of the basic slag produced at steel-works in this country was ground for agricultural use.[1] The farmer has indeed grown to depend on the steel industry, and the decline of the steel output which has followed the termination of the war—together with the extending use of fluorspar, which is prejudicial to the fertilizing quality of the slag—is a somewhat serious matter for British agriculture.[2]

It has been stated that even mineral phosphate, not treated with sulphuric acid, has a beneficial effect on pasture land, if only it be ground sufficiently finely.

Calcium Carbide (CaC_2). When calcium oxide is heated to a very high temperature with carbon, calcium carbide is formed by the reaction

$$CaO + 3C = CaC_2 + CO.$$

The reaction involves the absorption of a very large quantity of heat, and, like so many other endothermic changes, requires a very elevated temperature. Calcium carbide is in fact one of the most endothermic substances manufactured on a commercial scale. Up to the time when the introduction of the electric furnace provided an easy means of reaching very high temperatures, its existence was scarcely known.

Actually the reaction is a balanced one :—

$$CaO + 3C \rightleftharpoons CaC_2 + CO.$$

At any given temperature, there is a definite pressure of carbon monoxide corresponding to equilibrium. The change will take place from left to right until the pressure of carbon monoxide has reached this equilibrium value. At low temperatures an extremely low pressure of carbon monoxide is sufficient to stop further change. Even at 1,475° C. the equilibrium pressure is only 0·82 mm. of mercury. But at 1,840° C. it reaches one-third of an atmosphere, and at 1,920° C. it becomes equal to one atmosphere. Above this temperature, which is easily reached in the electric furnace, the formation of calcium carbide will proceed apace. It may be remarked, however, that a higher temperature than 2,000° C. is not desirable, since the carbide becomes decomposed to carbon and metallic calcium, which distils away.[3]

A carbide furnace consists essentially of a steel tank lined with refractory material containing the charge of lime and anthracite coal. Into this dip three stout carbon electrodes (often a foot or more in diameter) suspended from above, which are connected to a source of three-phase alternating current. The extremely strong current passing between them keeps the temperature very high, probably about 2,000° C., and calcium carbide is formed in the molten condition. Fresh lime and coal are added from time to time, and a portion of the carbide is run out through a tapping-hole, perhaps every 45 minutes, into a tray, where it quickly sets to a slab.

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[1] *J. Soc. Chem. Ind.* **36** (1917), 947.

[2] Sir A. D. Hall, *Trans. Faraday Soc.* **16** (1921), 283 ; Sir T. H. Middleton, *Trans. Faraday Soc.* **16** (1921), 275.

[3] M. de K. Thompson, "Applied Electrochemistry" (Macmillan), Chap. XII. See also M. de K. Thompson, *Met. Chem. Eng.* **8** (1910), 279, 324.

The problem of the tapping of carbide has constituted the main difficulty in the manufacture. Calcium carbide is very viscous just above its melting-point, and only becomes really fluid at very high temperatures; consequently there is a danger of the tapping-hole becoming choked. It is said that the presence of excess of lime increases the fluidity of the carbide. The difficulties connected with tapping have now been solved almost completely.

The action of the current is simply to heat the charge to the necessary temperature, which cannot be reached in any other way. There is no electrolysis, and therefore an alternating current can be used. The electrodes, which are red hot far above the top of the charge, are gradually eaten away; the provision of fresh electrodes is an important factor in the cost of carbide production.

The material obtained from the furnace is broken into lumps, and packed in drums. As usually produced, it is a greyish substance, which becomes incrusted with lime when exposed to damp air. Owing to the fact that the large amount of energy needed to bring about the formation of this endothermic substance is introduced in the form of electricity, the manufacture of carbide is mainly confined to places like Niagara where water-power is available for the cheap generation of electrical energy. It seems unlikely that the production of carbide will become successful in this country,[1] although carbide has been manufactured on a very big scale near Cologne (Germany), where a hard gas-coke is employed as the form of carbon.[2] An interesting feature of the process there conducted is the very large (rectangular) cross-section of the electrodes employed.

Calcium carbide is used in the generation of acetylene gas. When water is dropped on to the carbide, acetylene is generated,

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

Acetylene is a valuable illuminant, burning in air with a flame which is extremely bright, possibly owing to the presence of incandescent particles of unburnt carbon. The flame of acetylene burning in oxygen has an unusually high temperature owing to the endothermic nature of the gas. Consequently the oxy-acetylene blowpipe can be used in welding steel, and even for cutting iron-plates. A considerable quantity of carbide is now consumed in the manufacture of calcium cyanamide.

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[1] C. Bingham, *J. Soc. Chem. Ind.* **37** (1918), 85R.

[2] A. J. Allmand and E. R. Williams, *J. Soc. Chem. Ind.* **38** (1919), 304R.

Calcium cyanamide (CaN.CN) is made by passing nitrogen over finely ground calcium carbide heated at 1,000° C. The carbide should not be too pure, because free lime and other impurities lower the melting-point of the carbide and thus cause superficial fusion of the carbide grains—a state of affairs which aids the reaction with nitrogen.[1] The complete reaction can be written in the simple form,

$$CaC_2 + N_2 = CaCN_2 + C,$$

but it is probable that it really occurs in stages.[2] The reaction as a whole is exothermic.[3]

In the process as carried out at Niagara[4] the carbide, crushed and powdered until it passes through a 100-mesh sieve, is heated in small ovens in an atmosphere of nitrogen, which (in the latest plant) is prepared from liquid air. The finely powdered calcium carbide is extremely explosive, and has to be handled with great care. The temperature of the oven requires to be accurately regulated.

A great deal of cyanamide is also made in Germany, and, until recently, the Scandinavian output was very important.

Cyanamide is a most valuable nitrogenous fertilizer, and its introduction helped to dispel the fears which had formerly existed regarding the fate of agriculture in the day when the deposits of Chili nitrate come to be exhausted. The compound probably decomposes in the soil, yielding ammonia, which in turn becomes oxidized to nitric acid. The nitrogen can be assimilated readily by the crop only when it reaches the latter condition. Since both changes occupy time, cyanamide is clearly a slowly acting fertilizer, but the addition of cyanamide to the soil adds more to the permanent fertility than does a treatment with the more rapidly acting substances, such as sodium nitrate or ammonium sulphate.

On a much smaller scale, calcium cyanamide has been used as a case-hardener for steel. During the war, the manufacture of sodium cyanide from calcium cyanamide was commenced in

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[1] G. Bredig, W. Fraenkel and E. Wilke, *Zeitsch. Elektrochem.* **13** (1907), 69, 605.

[2] See A. J. Allmand's "Applied Electrochemistry" (Arnold).

[3] P. Dolch, *Zeitsch. Elektrochem.* **26** (1920), 455.

[4] W. S. Landis, *Met. Chem. Eng.* **13** (1915), 213.

America; the process has been referred to in the section on sodium.

Cyanamide can be used in the manufacture of ammonia and nitric acid. When heated under pressure in an autoclave with a solution containing calcium hydroxide and sodium carbonate, it yields ammonia gas, which may be allowed to pass out from the autoclave at a regulated rate.[1] Since nitric acid can be made by the interaction of ammonia and air in the presence of a catalyst, this provides a means of preparing nitric acid from atmospheric nitrogen by an indirect process.

Nitrogen + calcium carbide → Calcium cyanamide →
Ammonia → Nitric acid.

It is thought that this indirect method will prove, in countries where water-power is not very plentiful, a cheaper method of "fixing" nitrogen than the direct process of bringing about the combination of aerial oxygen and nitrogen by means of the electric arc; the direct process, which has been developed largely in Norway, may survive in places where electric power is exceptionally cheap. It is not certain, however, that the production of ammonia from cyanamide will prove as cheap as the production by the direct combination of hydrogen and nitrogen in the presence of a catalyst—a method which has been developed largely in Germany.

Plaster, Mortar and Cement

Plaster. When natural

Gypsum . . . . $CaSO_4.2H_2O$

is heated at a low temperature, say at 120° C., it loses most of its water, leaving the hemihydrate, usually known as

Plaster of Paris . . $2CaSO_4.H_2O$.

On further heating at a higher temperature (400°–1,000° C.) it loses the whole of the water, leaving a material which is practically identical in composition with natural

Anhydrite . . . $CaSO_4$.

Artificial anhydrite, however, differs from the natural mineral in possessing a "feathery" structure, and usually contains a little free oxide.[2] The anhydrous sulphate is often described as being *dead-burnt.*

When plaster of Paris is mixed with water, so as to form a plastic mass, it can be moulded into any form desired, and left to set. It very quickly sets to a firm and rigid mass of interlocking crystals of gypsum, due to recombination with water. The hemihydrate, usually mixed with some fibrous material, such as hair, tow, or wood-fibre, constitutes a useful material for plastering the internal walls and ceilings of living-rooms.

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[1] W. S. Landis, *Met. Chem. Eng.* **14** (1916), 87.

[2] R. Grengg, *Zeitsch. Anorg. Chem.* **90** (1914), 327.

On the other hand, the anhydrous sulphate, when mixed with water, sets far more slowly, but when at last it does set, a very hard mass is obtained. The rate of setting is considerably increased if it is finely ground, and it can then be used as a flooring-plaster.[1]

The preparation of plaster of Paris is usually carried out in muffle-ovens, as the temperature requires careful regulation. In Europe 110–130° C. is usual, but higher temperatures are employed in America, although the risk of producing a slow-setting plaster is thereby increased. For flooring-plaster, where a high temperature is needed, a vertical kiln can be employed, similar in principle to that used for burning limestone; care should be taken not to use too high a temperature, or to allow the heating to be too protracted, as the plaster may then be deprived entirely of its setting power. An English authority[2] recommends 400–500° C.

Whether plaster of Paris or flooring plaster is being made, the product is finely ground before being put on the market.

Theory of Setting of Plaster.[3] The setting process is most interesting from the theoretical standpoint. In contact with water, at ordinary temperatures, gypsum is the stable form of calcium sulphate, whilst both the anhydrous salt and the hemihydrate are metastable; in other words, they are more soluble than gypsum. Now plaster of Paris always contains a few unchanged particles of gypsum which have escaped dehydration. When a mixture of plaster of Paris and water is made, the water soon becomes saturated with the hemihydrate, and thus becomes supersaturated with respect to the gypsum. Therefore crystallization upon the gypsum particles occurs, and more hemihydrate dissolves, so as to keep the solution saturated. Consequently, the growth of the gypsum crystals continues, and the dissolution of the hemihydrate particles goes on, until the whole mass consists of interlocking gypsum crystals.

It should be pointed out that the fact that the crystals which have grown out from different nuclei do, as a fact, interlock or "dovetail," probably adds greatly to the strength of the plaster, although it has been shown, in the case of metals (Vol. I, Chap. I), that interlocking at the boundaries of the grains is not actually needed for the satisfactory cohesion of a granular mass.

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[1] L. A. Keane, *J. Phys. Chem.* **20** (1916), 701.

[2] E. B. Dancaster, "Lime and Cements" (Crosby Lockwood).

[3] C. H. Desch, *Trans. Faraday Soc.* **14** (1918–19), 1.

The setting of plaster is accompanied by an apparent expansion, and consequently, if a plaster-water mixture is allowed to harden in a mould, a very sharp impression is obtained, all the indentations of the mould being accurately reproduced. Yet actually, on comparing the specific volumes of gypsum with those of the hemihydrate and water, one would expect a contraction to accompany the process of hydration. This apparent discrepancy is explained by the fact that the mass produced through the "setting" is porous. The crystals growing out from different points do not extend uniformly in all directions, and are possibly dendritic in character. Apparently the crystals growing out from different nuclei meet at certain points, and thrust apart one another, thus causing the expansion of the whole mass. When setting is complete, the neighbouring crystallites are in contact at some points, but not at others; thus cavities exist in the material.

In the setting of dead-burnt (flooring) plaster,[1] this apparent expansion is not observed, and consequently the mass is harder and less porous. It is to be expected that after the drastic heating at a high temperature there would be few, if any, gypsum particles surviving which could act as nuclei; hence the slower rate of setting is easily understood.

Various substances can be added to plaster to increase or decrease the rate of setting. One would imagine that, in general, substances which increase the solubility of calcium sulphate would increase the rate of setting, and that those that decrease the solubility would decrease the rate; in spite of some exceptions,[2] this rule generally holds good. Sodium sulphate is sometimes added to strongly burnt plaster to increase the rate of setting, whilst sodium chloride is also employed as an accelerator. On the other hand, colloidal substances—and others which would increase the viscosity—generally reduce the velocity of crystallization and act as retarders. Glue is often added to retard the setting of plaster, whilst alum and borax have a similar effect.

Lime Mortar. Another composition which is plastic when first mixed but which sets to a hard mass is the lime mortar used by builders. This consists essentially of a mixture of slaked lime, sand and water. The setting of mortar is a fundamentally different process from that of plaster. No hydration is involved since the lime is fully hydrated (slaked) before being mixed with the sand and water. According to Desch,[3] the hardening process is analogous to the setting of a plastic clay on drying, or to the hardening of a silica gel; probably the particles of calcium hydroxide, which are of very small (colloidal) size, become bound together by direct molecular forces such as are involved in the union of the particles of typical "sticky" colloids. The function of the sand is simply to prevent cracking "by subdividing the lime into thin layers." Slaked lime shrinks very much when it dries, and if the sand were omitted cracks would appear in the mass. After the primary setting, further changes may take place in the mortar, such as the conversion of hydroxide to carbonate, but this conversion adds much less to the strength of the mortar than is commonly supposed.

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[1] C. H. Desch, *Trans. Ceram. Soc.* 18 (1918–19), 15.

[2] C. L. Haddon, *J. Soc. Chem. Ind.* 39 (1920), 165T; 40 (1921), 123T.

[3] C. H. Desch, *Trans. Faraday Soc.* 14 (1918–19), 4. See also C. H. Desch, "Chemistry and Testing of Cement" (Arnold), 1911 Edition, page 109.

Portland Cement.[1] Cement is a more complicated substance than either plaster or mortar. It consists essentially of a mixture of silicates and aluminates of calcium in a finely powdered form. When mixed with water, it sets to a hard compact mass, owing to a hydration process not dissimilar from that responsible for the setting of plaster.

Cement is formed by heating an intimate mixture of clay (aluminium silicate) and powdered calcium carbonate to incipient fusion. The calcium carbonate loses carbon dioxide, and the lime produced reacts with the two components of the clay to produce the aluminate and silicate of calcium,

$$5CaO.3Al_2O_3$$
$$2CaO.SiO_2$$

These two substances are produced at comparatively low temperatures, but when the particles begin to fuse upon the surface, they take up further lime and the compounds

$$3CaO.Al_2O_3$$
$$\text{and } 3CaO.SiO_2$$

are produced; the first of these compounds is considered by some chemists[2] to be a solid solution of CaO in $5CaO.3Al_2O_3$. It is most important that this further absorption of lime should take place, since the compound $3CaO.SiO_2$ is the essential component of cement. If the charge contained no impurities, the superficial fusion needed for the formation of $3CaO.SiO_2$ would not take place below 1,650° C.; but, owing to the impurities present in ordinary materials, a burning temperature of 1,300–1,350° C. will usually suffice to give good cement.[1] A typical cement of satisfactory quality contains the three compounds

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[1] C. H. Desch, "Chemistry and Testing of Cement" (Arnold); B. Blount, "Cement" (Longmans, Green), 1920.

[2] E. D. Campbell, *J. Ind. Eng. Chem.* 9 (1917), 943.

$$3CaO.SiO_2$$
$$2CaO.SiO_2$$
$$\text{and } 3CaO.Al_2O_3$$

The raw materials for cement manufacture are essentially

(1) *limestone*, as the source of calcium oxide,

and (2) some sort of *clay* (which may be in the form of hard shale or soft clay-mud), as a source of alumina and silica. Some naturally occurring materials contain both the essential ingredients, although not necessarily in the desired proportions; for instance, chalk marl is limestone containing some argillaceous matter.

The materials must first be intimately mixed, and very finely ground, the grinding usually being conducted in a ball-mill. It is

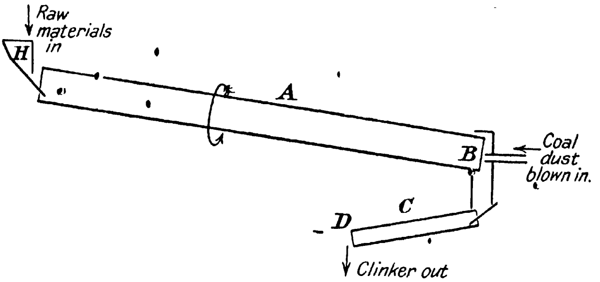

FIG. 15.—Rotary Cement Kiln.

then "burnt" in a kiln or furnace. Many forms have been employed, but the revolving furnace shown in Fig. 15 has generally proved the most suitable.[2] The long tube A (often more than 200 feet long) is set at a slight incline, and revolves slowly (1 to 2 revolutions per minute). The raw materials, which need not be previously dried, are introduced at H, and gradually work along the tube; as they approach the lower end the temperature rises higher and higher. The fuel employed is usually powdered coal, which is blown in at B by means of a fan. At B the calcined material which now consists of well-burnt "clinker" drops into the lower tube C, in which it is cooled by the draught of air passing in the opposite direction. The clinker emerging from D is again ground in ball-mills, and is ready for use. The cement dust passing out with the emergent gases is often led through a dust-catcher, and possibly through an electrostatic precipitation plant with a view to the recovery of the potash.

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[1] A. A. Klein, *Trans. Faraday Soc.* **14** (1919), 14.
[2] E. D. Boyer, *J. Soc. Chem. Ind.* **37** (1918), 19T.

Theory of Setting of Cements. Essentially, the setting of cement is a hydration process similar to that of plaster. The most important constituent of cement, $3CaO.SiO_2$, if tested alone, combines with water, setting in 5 hours to a strong mass of hydrated silicate, containing also some crystalline calcium hydroxide.[1] The hydrated silicate appears to be amorphous when viewed under the microscope; but this may be because the crystal growths are of too small a size to be observed.[2] There is no reason to assume that the process is necessarily different from the process of the setting of plaster.

The other constituents of the cement also combine with water, but add little to the practical value of the cement. The silicate $2CaO.SiO_2$ sets so slowly as to be of little service for the first few weeks, whilst the aluminate $3CaO.Al_2O_3$ quickly becomes hydrated, but the product has little strength.

Some authorities consider that gelatinous silica is the real binding agent, which cements the constituent grains to one another.[3] This is formed—according to these authorities—by the hydrolysis of the silicates (especially the quickly-setting $3CaO.SiO_2$), and is probably of a colloidal character; the gel subsequently hardens, just as does glue or other organic gel, binding the grains together. The theory, as put forward, is perhaps a little vague; but it seems probable, from a microscopic examination of natural sandstones, that the crystalline sand-grains composing those rocks are bound together by an apparently "amorphous" form of silica, and it is not unreasonable to suppose that the same substance may act as a binder in the setting of cements.

There has been a considerable amount of controversy regarding the mechanism of setting; some authorities believe that the grains become bound together by a colloidal substance, others by a fine crystalline ground-mass. The controversy does not concern cement alone, since a colloidal theory of the setting of plaster has found many advocates.[4] If, however, we accept von Weimarn's view that even a gel consists of minute crystals, the two theories become practically identical—and the controversy reduces to a mere disagreement regarding the probable size of the crystalline particles.[5]

Employment of Cement. Cement may be employed mixed with sand in "cement mortar"; or, with the addition of gravel also, as "concrete." In addition to the older uses of concrete in constructional work, concrete blocks are now manufactured as a standard building-material, whilst the ferro-concrete type of building is erected frequently in the centre of large towns.

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[1] A. A. Klein, *Trans. Faraday Soc.* **14** (1919), 21.
[2] H. Le Chatelier, *Trans. Faraday Soc.* **14** (1919), 10.
[3] G. A. Rankin, *Trans. Faraday Soc.* **14** (1919), 23.
[4] J. Traube, *Koll. Zeitsch.* **25** (1919), 62.
[5] E. Hatschek, *Trans. Faraday Soc.* **14** (1919), 53.

The quantity of sand which can be employed in a mixture without unduly reducing the strength of the material obtained upon setting varies rather with the fineness of the cement. Recent investigations have tended to show that the coarser particles ("grit") of a cement take little or no part in the setting; the value of a cement is due to the fine particles ("flour").[1] If, therefore, a cement consists mainly of flour, it can probably be diluted with a comparatively large proportion of sand, and yet produce a sound material after setting.

Other Types of Cement. Besides Portland cements, numerous other siliceous substances are found to have setting properties. **Hydraulic lime** made by burning argillaceous (clayey) limestone has already been mentioned; it can be employed in cement mixtures. Various rocks of volcanic origin (known as puzzolanic materials) found in the volcanic districts of Italy, Greece and the Eiffel, are employed, in the finely ground state, as **natural cements.** They are rich in alumina and silica; as a rule, it is necessary to mix lime with these materials before they assume good setting properties but no burning is necessary. Ancient Roman Cement was a volcanic product of that character, but the name **Roman Cement** has—in recent times—been applied to a product obtained by burning the "septaria nodules" consisting of clay and chalk, which are found in Sheppey and elsewhere; the name has also been applied to materials produced by burning other forms of clay limestone. Roman Cement sets quicker than Portland Cement, and is still used to some extent for work under water. There is no sharp distinction between hydraulic limes and Roman Cement, whilst some of the natural cements produced in America have practically the same composition as Portland Cement.

Blast-furnace Slag, a bye-product of the manufacture of pig-iron, consisting largely of calcium silicate, has acquired a very great importance in the cement industry. Almost any blast-furnace slag may be used as the source of calcium and silica in mixing up the raw materials required for Portland Cement. But some slags can actually be ground without further burning, and added to ordinary Portland Cement to give the so-called "Iron Portland

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[1] Compare T. Hattori, *J. Chem. Ind. Tokyo*, 20 (1917), 1018; abstract *J. Soc. Chem. Ind.* 37 (1918), 59A.

Cement" which is often stronger than Portland Cement undiluted with slag.[1]

Slags from other metallurgical industries cannot be used for cement-making as they contain sulphides; the presence of sulphides greatly diminishes the strength of cement.

The following table, which represents a summary of various analyses quoted by Desch and others, is intended to give a rough idea of the percentages of the five main oxides occurring in the more important types of cements or cement-like materials; they must not be regarded as fixing the outside limits between which the composition of the different materials varies.

	Portland Cement (English, American and German).	"Natural Cement" (American)	"Puzzolana" (Italian) (without addition of Lime.)	"Roman Cement" (Sheppey or Harwich).	Hydraulic Lime (English or French).	Blast-furnace Slag.
CaO	60–64	33–54	10–12	46–48	63–74	44–52
SiO_2	20–24	22–26	46–48	17–25	14–21	27–35
Al_2O_3	5–10	7–12	17–19	4–7	1–7	8–20
Fe_2O_3	2–4	2–5	3–11	9–12	1–3	
MgO	1–3	2–20	2–3	2–4	0·7–1·5	0·6–2·5

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[1] E. H. Lewis, *J. Iron Steel Inst.* **101** (1920), 111.

STRONTIUM

Atomic weight 87·63

The Metal

Strontium is the next metal of the group. The properties of the element and compounds are very similar to those of calcium and the calcium compounds; the differences which are observed are such as would be expected from a consideration of the Periodic Table.

Strontium is a white metal, heavier than calcium, the specific gravity being 2·54; it is softer than calcium and can be cut with a knife. It melts at 800° C. and is appreciably volatile just above the melting-point.

The metal decomposes water with violence, and burns, when heated in air, with a bright flame, a mixture of oxide and nitride being produced. When exposed to damp air at ordinary temperatures, it rapidly loses its metallic lustre.

Laboratory Preparation. The metal can be obtained by the electrolysis of the fused chloride. The device of a gradually rising cathode, adopted in the case of calcium, does not work well for the preparation of strontium, as the metal does not adhere readily to the cathode.[1] It is best to conduct the electrolysis in an iron pot which serves as cathode, a carbon rod being employed as anode. The use of a vessel lined with fireclay or other silicate is detrimental to smooth working, as a non-conducting film of silica appears on the anode.[2]

Strontium is, of course, too reactive for separation from an aqueous solution, but when a solution of strontium chloride in water is electrolysed with a mercury cathode, a strontium amalgam is obtained.[3] When this amalgam is heated *in vacuo*, most of the mercury passes off as vapour, and the less volatile strontium is left behind. But in order to drive off the whole of the mercury it is necessary to heat the product still more strongly in a current of hydrogen; under these conditions, strontium hydride is formed, which itself decomposes on further heating, yielding strontium and hydrogen.

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[1] B. L. Glascock, *J. Amer. Chem. Soc.* **32** (1910), 1222.

[2] K. Arndt and K. Willner, *Ber.* **40** (1907), 3025.

[3] A. Guntz and G. Roederer, *Bull. Soc. Chim.* **35** (1906), 494, 503.

Compounds

Strontium oxide, SrO, is formed when strontium burns in oxygen. Like quicklime, it is a white infusible mass; it combines rather more readily with water than calcium oxide, and the **hydroxide,** $Sr(OH)_2$, produced is somewhat more soluble than slaked lime; the solution is alkaline. Strontium oxide has more strongly basic properties than calcium oxide; it is, in consequence, more difficult to prepare the oxide by heating the carbonate. If it is desired to prepare strontium oxide from strontium carbonate, it is best to heat the latter with a little carbon, the reaction

$$SrCO_3 + C = SrO + 2CO$$

occurring at a comparatively low temperature.

Salts. The strontium salts are closely analogous to those of calcium, but in general are less soluble. The **chloride,** $SrCl_2$, is very soluble in water, but not so soluble as calcium chloride; the anhydrous salt is scarcely deliquescent. It is moreover insoluble in alcohol, which freely dissolves the calcium compound; several hydrates are known. The **nitrate,** $Sr(NO_3)_2$, although soluble in water, is almost undissolved by concentrated nitric acid.

Strontium sulphate, $SrSO_4$, is less soluble than calcium sulphate, just as calcium sulphate is less soluble than magnesium sulphate. Strontium sulphate is, in fact, practically insoluble in water containing a little alcohol. It is prepared in the usual way by adding a soluble sulphate to a soluble strontium salt, and comes down as a rather heavy white precipitate. The **carbonate** and **phosphate** are other insoluble salts obtained by precipitation.

The **nitride, hydride** and **peroxide** of strontium are prepared in the same way as the corresponding calcium compounds, which they resemble in general properties.

Analytical

The red coloration imparted to a Bunsen flame by strontium compounds can be used to detect the metal. The sample to be tested should be moistened with hydrochloric acid, so that the chloride, a comparatively volatile compound, may be formed.

The spectrum afforded by a flame containing strontium gives a certain means of distinguishing the metal from others which produce a red colour, and of recognizing it in the presence of other substances which impart a colour to the flame. The spectrum of strontium includes several characteristic lines in the red and orange-yellow, and one in the blue region.

Like calcium on the one hand, and barium on the other, strontium gives no precipitate with hydrogen sulphide, ammonia (in the presence of ammonium chloride) or ammonium sulphide. The three metals are, however, precipitated by ammonium carbonate. The separation of strontium and barium from calcium has already been discussed; various methods are known, depending on the superior solubility of the nitrate or sulphate of calcium in various reagents. The separation of strontium from barium has still to be considered. If the strontium and barium are present as sulphate—which is usually the case after the separation of calcium—these mixed sulphates can be boiled for some time with ammonium carbonate.[1] This process converts the strontium sulphate into strontium carbonate, which is actually a less insoluble salt than the sulphate. Barium sulphate is, however, too insoluble to suffer this transformation. Therefore, when the residue is treated with dilute nitric acid, the strontium carbonate will be decomposed, the whole of the strontium passing into the form of soluble nitrate, but the barium sulphate will remain unchanged and can be filtered off.

Another method for the separation of barium and strontium depends on the insolubility of barium chromate.[2] The solution containing the metals as nitrates or acetates is first made alkaline with ammonia, and then weakly acidified with acetic acid. Excess of ammonium chromate is then added, when the barium will be completely precipitated as chromate, whilst the strontium remains in solution.

When once a solution of a strontium salt free from other metals has been obtained, the strontium can again be precipitated by ammonium carbonate; the precipitate of strontium carbonate is filtered off, washed, ignited gently and weighed. Strontium can also be precipitated as sulphate, which is practically insoluble in a solution containing a little alcohol. The strontium salt solution is in this case treated with a little alcohol and a slight [illegible] of sulphuric acid; the precipitate is filtered off, washed with dilute alcohol, dried and weighed as strontium sulphate. But the precipitation of strontium as sulphate in the presence of alcohol is not advisable if the solution contains chromates; when those compounds exist in the solution, the strontium is preferably thrown down as carbonate, which may, if desired, be converted to sulphate afterwards.

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[1] Sir W. Crookes, "Select Methods in Chemical Analysis" (Longmans), 1905 Edition, p. 46.

[2] R. Fresenius, *Zeitsch. Anal. Chem.* **29** (1890), 413. A method of separating barium, strontium, and calcium from one another, depending on the differences in the solubilities in the three chromates is described by I. M. Kolthoff, *Pharm. Weekblad,* **57** (1920), 1080; Abstract *J. Chem. Soc.* **120** (1921), ii. 63.

TERRESTRIAL OCCURRENCE

Strontium occurs only in small quantities in igneous rocks; it appears to be expelled to some extent in the thermal waters given off in the later stages of the consolidation of an intrusive mass. Thus strontium is a constituent of many mineral springs.

Deposits of the less soluble strontium salts, notably the sulphate

Cœlestine . . . . . $SrSO_4$

and the carbonate

Strontianite . . . . . $SrCO_3$

occur in many parts of the world. The former often forms fine rhombic crystals of prismatic habit. Some of the deposits of strontium minerals are found in veins, and have evidently been deposited by thermal waters arising from an igneous mass lower down. The more important deposits are, however, of secondary origin. It is probable that waters percolating from above have dissolved the original strontium minerals from the veins, and have deposited them at other places where the conditions were favourable. Dissolved carbon dioxide probably has favoured the dissolution. Where the percolating waters have entered a bed of limestone, the free carbon dioxide has ceased to exist in the water, and the strontium mineral has been dropped. Thus we often find strontium minerals associated with limestone—e.g. in Michigan.

Near Bristol (England) there is an important deposit of cœlestine consisting of lenses and veins in the red marls of Triassic age. Other British deposits of strontium compounds occur in Yorkshire and Argyllshire. Cœlestine is found in Sicily in association with gypsum and sulphur; the mode of origin is still somewhat doubtful.

TECHNOLOGY AND USES

Both the sulphate and carbonate are used as sources of soluble strontium salts. The latter can readily be converted to nitrate by the action of nitric acid. But the former must first be reduced to sulphide by heating with coke. From a solution of the sulphide the strontium can be precipitated as carbonate by carbon dioxide gas. The nitrate, and also the refined carbonate, are the chief forms in which strontium comes on the market. The oxide can be made by igniting the carbonate in gas-fired furnaces, a high temperature being needed.

The practical importance of strontium is due to the fine red colour which it confers upon a flame; it is employed in fireworks, as well as in the light-signals used in warfare, and in connection with aviation.

A little metallic strontium—obtained by the electrolysis of the fused chloride—is said to be used in America as a deoxidizer for copper castings.

Strontium hydroxide has also proved useful in the extraction of sugar from syrups and molasses which—owing to the presence of impurities—do not readily crystallize. This process was largely developed in Germany. The molasses are boiled with strontium hydroxide solution, and on cooling the rather insoluble strontium saccharate (or sucrate) crystallizes out. This can be removed by filter-pressing and decomposed by means of carbon dioxide, liberating sugar in a comparatively pure form, which crystallizes without difficulty.

At the present time, however, lime is to a large extent used instead of strontia for this purpose; in America, until lately, strontia had never been used for sugar refining, but—in recent years—experiments in the refining of sugar with strontium have been carried out.[1]

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[1] G. W. Stose, *U.S. Geol. Surv., Min. Res.* (1919), II, 95.

BARIUM

Atomic weight 137·37

The Metal

Barium bears the same relation to strontium as the latter bears to calcium. The element is a silver-white metal, melting and boiling at a slightly higher temperature than strontium. It is considerably heavier than the preceding members of the group, the specific gravity being 3·8. The salts, it may be mentioned, are even heavier, the sulphate having a specific gravity, varying in different forms from 4·3 to 4·5 ; hence the derivation of the name (βαϱυς = heavy).

Barium is more reactive than strontium or calcium, and decomposes water even more vigorously ; the comparative rapidity of the reaction is due not only to the lower position of the metal in the Potential Series, but also to the greater solubility of the hydroxide. Metallic barium exposed to the damp atmosphere is quickly attacked. It burns readily in air.

Laboratory Preparation. The metal can be prepared by the electrolysis of the fused chloride (with, or without, the addition of fluoride), but it is preferable to obtain it through barium amalgam, in the way described for the preparation of strontium. When an aqueous solution of barium chloride is electrolysed with a mercury cathode, an amalgam is obtained, which, when distilled in a current of hydrogen at 950° C. yields barium.

Compounds

Barium oxide (*Baryta*), BaO, formed when barium burns in oxygen, is a white substance, which can only be fused in an electric furnace, and becomes incandescent when heated. It combines with water with great evolution of heat—greater than was observed in the case of calcium or strontium oxide. **The hydroxide**, $Ba(OH)_2$, so produced is more soluble than the hydroxides of the previous members of the group, but the saturated solution only contains 3·9 per cent. $Ba(OH)_2$ at 20° C. The solution, known as *baryta-water*, is strongly alkaline, and readily absorbs carbon dioxide.

Since barium oxide is more strongly basic than the oxides of calcium or strontium, it is to be expected that the decomposition of the carbonate into barium oxide and carbon dioxide

$$BaCO_3 = BaO + CO_2$$

will only occur at a very high temperature. As a matter of fact this reaction requires a white heat, but the oxide can be prepared at a lower temperature by heating the carbonate with carbon,

$$BaCO_3 + C = BaO + 2CO.$$

Salts. The salts of barium are heavy colourless substances. The **chloride** is prepared in a hydrated form, $BaCl_2.2H_2O$, by crystallization. The anhydrous salt is obtained by heating the hydrate; it is not deliquescent, and is rather less soluble than strontium chloride. The chloride is slowly hydrolysed by a current of steam, hydrogen chloride being carried off; the residue contains free hydroxide and can be shown to be alkaline. The **nitrate** is less soluble than strontium nitrate. The chloride and nitrate are almost insoluble in concentrated hydrochloric and nitric acids respectively. They can be precipitated, therefore, from strong solutions by addition of these reagents.

Barium sulphate, $BaSO_4$. The insolubility of the sulphate is more pronounced in the case of barium than in the lower metals of the group. Barium sulphate is produced as a very fine but heavy powder when a soluble barium salt is added to a soluble sulphate. In this respect, barium resembles lead, which also forms a heavy insoluble sulphate. The exceptionally fine nature of the precipitate appears to be due to the great degree of supersaturation produced when the solutions of the barium salt and the sulphate are mixed; this high degree of supersaturation causes nuclei of barium sulphate to be formed at a very large number of points in the solution. As stated in Chapter VI (Vol. I), the minute crystals produced cling together to form apparently amorphous aggregates. The work of von Weimarn has shown that at greater dilutions, where the degree of supersaturation is less, star-shaped crystal skeletons, and even well-formed geometrical crystals are produced, and these can be observed when the precipitate is examined under the microscope.[1]

If the right conditions are obtained, it is even possible to produce crystals of barium sulphate of size visible to the naked eye.[2] A small evaporating dish containing a little barium chloride is placed in a much larger dish, and a little sodium sulphate solution is placed in the annular space between the dishes, water being very cautiously added to both dishes until the small dish is completely submerged; the large dish is then left for some months in a place of uniform temperature. The salts gradually diffuse upwards, and meet one another in a very dilute solution, so that the degree of supersaturation is very small. As a result, few crystal nuclei appear spontaneously, and the slowly grown crystals are of large size, resembling natural barium sulphate (*barytes* or *heavy spar*). This is interesting, as it suggests that the mineral barytes also has been formed by very slow crystallization from very low dilution.

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[1] P. von Weimarn, *Koll. Zeitsch.* 3 (1908), 282.

[2] O. Lehmann, "Molekular Physik" (Engelmann), 1888 edition, Vol. I, page 514.

If an ordinary fine precipitate of barium sulphate is allowed to stand in the presence of boiling water containing hydrochloric acid, the fine barium sulphate becomes changed to a coarser variety of precipitate. The explanation commonly given is that the bigger crystals grow while the small ones, which are more soluble, are dissolved and disappear. But, as already stated in Chapter VI (Vol. I), it is more probable that the growth depends mainly on the adhesion of the small particles to form secondary aggregates; the process can be regarded as analogous to the flocculation of a colloidal solution.[1]

It is noteworthy that the precipitate of barium sulphate obtained by the interaction of barium chloride and sulphuric acid is rather less fine when sulphuric acid is present in excess at the moment of precipitation than when barium chloride is in excess. An explanation of this fact, based on the peptizing power of the various adsorbed ions, has been suggested.[2]

It has been explained above that, by using exceptionally dilute solutions, barium sulphate can be obtained in a visibly crystalline form. If we pass to the other extreme, and use extremely concentrated solutions, another unfamiliar form of precipitate is obtained. Von Weimarn, using the two exceptionally soluble salts, barium thiocyanate and manganese sulphate, was able to prepare solutions of 5–7 N concentration. He found on mixing such solutions that barium sulphate is thrown down as a gelatinous precipitate. Here the degree of supersaturation was, naturally, exceptionally high, and the particles produced were of colloidal size.

A colloidal solution of barium sulphate, of a fairly stable character, is obtained by the interaction of a sulphate and a barium salt in the presence of casein, which appears to act as a protective colloid.[3] A slightly alkaline solution of sodium sulphate containing casein is mixed with a concentrated solution of barium chloride, a thick, creamy liquid being obtained. The addition of acetic acid causes a curdy precipitate, which can then be washed free from other salts. The product yields a colloidal solution when stirred with water containing a trace of caustic alkali. The liquid obtained passes unchanged through filter-paper, and is perfectly transparent when viewed by transmitted light, although milky when viewed by reflected light. On evaporation it gives a horny translucent solid, which again yields the colloidal solution when treated with water containing alkali.

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[1] Compare the views of S. Odén, *Svensk. Kem. Tidskr.* **32** (1920), 108; Abstract, *J. Chem. Soc.* **120** (1921), 25.

[2] By H. B. Weiser, *J. Phys. Chem.* **21** (1917), 314.

[3] E. Feilmann, *Trans. Faraday Soc.* **4** (1908), 175.

Barium carbonate is obtained as a heavy precipitate when a barium salt solution is treated with soluble carbonate; it is to some extent soluble in water containing carbon dioxide. The **phosphate** is also insoluble, but, like most phosphates, is dissolved by mineral acids.

Barium Sulphides. When hydrogen sulphide is passed over heated barium oxide, the sulphide, BaS, is formed. The same substance is produced by heating barium sulphate with carbon. When the materials are not too pure, it is found that the product has usually the property of phosphorescence, noticed in the case of calcium sulphide.

When barium sulphide is treated with water, it is decomposed, forming the **hydrosulphide**, $Ba(HS)_2$, and hydroxide, $Ba(OH)_2$, both of which are soluble. This decomposition of barium sulphide by water proceeds more quickly than the corresponding interaction of calcium sulphide with water. The hydrosulphide is also formed when a solution of barium hydroxide is saturated with hydrogen sulphide; it crystallizes in colourless needles having the composition $Ba(HS)_2.4H_2O$. Various **polysulphides** have been described.

Lower Salts. When fused barium chloride is electrolysed, it is noticed that the barium formed at the cathode is somewhat soluble in the bath. The salt round the cathode is found on cooling to have the power of decomposing water with evolution of hydrogen. This has been attributed to the presence of a sub-chloride ($BaCl$). But a similar phenomenon has been met with in the electrolysis of calcium, sodium and potassium chlorides, and is thought by most chemists to be due to particles of the metal dispersed as a "fog" throughout the mass of salt. It is natural to suggest that a similar explanation may hold good in the case of barium. A lower oxide, Ba_2O, corresponding to the sub-chloride, has also been described. It is said to be formed when barium oxide is strongly heated with metallic magnesium; the magnesium abstracts part of the oxygen, and leaves a dark mass which decomposes water with the evolution of hydrogen. But here again, one cannot refrain from suggesting that the dark mass may consist of an intimate mixture of metal and oxide.

Barium hydride is formed when barium or its amalgam is heated at 1,400° C. in a current of dry hydrogen. It decomposes water, hydrogen being evolved.

Barium nitride, Ba_3N_2, is obtained when nitrogen is passed over heated barium or barium hydride. It is a yellowish substance decomposed by water with the production of ammonia and barium hydroxide.

By the action of ammonia gas on barium at low temperatures (e.g. $-20°$ C.) a reddish solid with the composition $Ba(NH_3)_6$ is obtained; but at ordinary temperatures it readily loses ammonia and hydrogen yielding the whitish amide, $Ba(NH_2)_2$.[1] The amide yields barium nitride on heating.[2]

Barium peroxide. When barium oxide (BaO) is heated in a stream of oxygen to dull redness, the peroxide, BaO_2, is formed. If the peroxide is heated more strongly, it decomposes again, but this decomposition is prevented if the heating is conducted under pressure. At any temperature there is a definite pressure of oxygen at which barium oxide and peroxide will be in equilibrium.

$$2BaO + O_2 \rightleftharpoons 2BaO_2.$$

If the oxygen pressure be less than this amount, the peroxide will decompose, yielding the oxide. If it is greater, the oxide will be converted to the peroxide. The decomposition pressure becomes equal to the pressure of the atmosphere at 795° C., and consequently above that temperature barium peroxide contained in an open vessel decomposes extremely rapidly.[3]

A hydrated form of the peroxide is obtained when hydrogen peroxide is added to baryta-water; a crystalline precipitate having the composition $BaO_2.8H_2O$ is produced. A compound with hydrogen peroxide, $BaO_2.H_2O_2$, is also known; this compound, which is at first colourless, becomes yellow when preserved at ordinary temperatures.[4] The colour change has been attributed to the formation of a higher oxide, BaO_4, but the matter appears still to be a little doubtful.

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[1] W. Biltz and G. F. Hüttig, *Zeitsch. Anorg. Chem.* **114** (1920), 241.

[2] Mentrel, *Comptes Rend.* **135** (1902), 740.

[3] J. A. Hedvall, *Zeitsch. Anorg. Chem.* **104** (1918), 163.

[4] W. Traube and W. Schulze, *Ber.* **54** (1921), 1626.

Analytical

Barium compounds impart a yellowish-green coloration to a Bunsen flame, and this can be used in the detection of the metal. The substance to be tested should be moistened with hydrochloric acid. If the barium flame is observed through a spectroscope a large number of lines are observed, distributed over the spectrum. Of these, three of the green lines are the most distinct.

In aqueous solutions, barium salts behave very similarly to those of calcium and strontium. The methods of separating barium from strontium and calcium have already been described. The most usual method depends on the relatively small solubility of barium chromate. Barium can be weighed as the chromate ($BaCrO_4$), which is not decomposed by gentle heating. After drying at 110° C., it still contains 0·5 per cent. of moisture, for which allowance should properly be made.

If a solution containing barium salts alone can be obtained, it is preferable to precipitate the barium as sulphate. As usually produced the precipitate of barium sulphate is so fine that it passes through ordinary filter-paper. Special filter-paper can be obtained which retains the fine sulphate, but the washing of the precipitate on such a filter is somewhat slow. It is, moreover, possible, by taking the proper precautions, to obtain the sulphate in a coarser form which does not pass through the pores of ordinary filter-paper. If the boiling barium salt solution containing ammonium chloride and a trace of free hydrochloric acid, be treated with boiling dilute sulphuric acid, and if the mixture is boiled for a few minutes and allowed to stand in a warm place for some time, the precipitate will be found to have settled to the bottom in a dense form, the filtration of which presents no difficulty. The sulphate must be carefully washed, since it is very apt to adsorb soluble salts; it is then dried, gently ignited and weighed.

Terrestrial Occurrence

Barium is found in small quantities in igneous rocks, mainly as a minor constituent of felspar and micas. The average content of igneous rocks is said to be about 0·1 per cent. Evidently, like most comparatively rare elements, it has tended to accumulate in the last-solidifying portions of the igneous mass, and has been largely expelled in solution in the waters which are given off by the mass during the final stages of consolidation. Thus we find

Barytes (heavy spar) . . $BaSO_4$

commonly deposited in mineral veins along with other vein-minerals; it is, for instance, often associated with lead and zinc ores. The barytes often occurs in large well-developed rhombic crystals, the size of which would seem to indicate that the compound must have been deposited very slowly from dilute solutions, in which the solubility was not greatly exceeded. Part of the barium held in solution by thermal waters is sometimes retained until the waters reach the earth's surface, and accordingly the waters of many mineral springs have a considerable content of barium salts.

As in the analogous case of strontium, the more important deposits of barium minerals are of secondary origin. Barytes is quite perceptibly soluble in water containing carbon dioxide, and this has probably been an important factor in the leaching of the primary barytes from mineral veins by infiltrating waters. If, however, the waters meet with large quantities of soluble sulphates, barytes will again be deposited; thus it is not surprising to find barytes crystals in pyritic shales, the sulphates being provided by the weathering of pyrites.[1] Likewise, the existence of barytes in limestone—which would tend to remove carbon dioxide from the waters—is easily understood. In some places, where the limestone itself has afterwards been eaten away by the action of water, considerable concentration of barytes has occurred.

Quite important deposits occur in the north of England, especially in Cumberland and Westmorland, but purer and whiter barytes occurs in Germany. Much barytes is mined in the United States, notably in Georgia, Missouri and Tennessee. The Missouri deposits are probably of a primary character, having been deposited directly from waters rising from an igneous mass.[2]

Another barium-containing mineral is the carbonate

Witherite	$BaCO_3$,

which is also found in this country.

TECHNOLOGY AND USES

The salts of barium can be made from witherite by the direct action of acid. If barytes is used as the source of barium, it is first reduced by heating with coal to the sulphide (BaS), which can afterwards be dissolved in any acid required.

Various *pigments* contain barium. The precipitated sulphate is, by itself, not satisfactory for ordinary use in painting; but by precipitating barium sulphide with zinc sulphate solution, the valuable pigment **lithopone**[1] is obtained,

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[1] C. W. Dickson, *Sch. Min. Quart.* **23** (1902), 366.

[2] W. A. Tarr, *Econ. Geol.* **14** (1919), 46.

$$BaS + ZnSO_4 = BaSO_4 + ZnS.$$

It happens that both the products of this double decomposition are insoluble and the precipitate is, therefore, a mixture of barium sulphate and zinc sulphide. It must be heated to redness in a muffle-furnace, quenched with water and ground, before it is fit for use. The quenching serves to break up the particles, and thus increases the whiteness and the covering power. Lithopone is a comparatively cheap pigment, and is much used for flat wall paints and the cheaper grade of enamel paints. The chief disadvantage is a tendency to darken when exposed to light, which has been proved to be due to the formation of metallic zinc from the zinc sulphide.[2] In the dark, the paint recovers its whiteness, the zinc being converted to oxide by the action of the air. Various samples of lithopone, differing in composition and in the method of manufacture, vary considerably in their tendency to blacken; it is stated that lithopone which is quite free from zinc chloride is perfectly stable to light.[3]

Precipitated barium sulphate is considerably used for the facing of white paper. The whitest and purest product is used for this purpose. In the manufacture of photographic printing-paper, baryta-coated paper is nearly always employed, and some embarrassment was caused in this country at the commencement of the war, owing to the fact that this type of paper had previously been imported from Germany. Probably German makers will always have a natural advantage in making baryta-coated paper on account of the comparative purity of the raw material found in their country.

Barium sulphate is also used in paints, as an inert "filler," mixed with the white lead or zinc oxide which constitutes the pigment-material proper. It is also used in coloured paints to dilute the colouring matter. For admixture with white pigments, only the precipitated sulphate should be used; natural barytes, however, finely ground, is practically useless. There is, of course, a temptation to add the cheap natural form of the compound. Ordinary chemical analysis will not detect the adulteration, but microscopic examination of the paint will reveal it.[4]

On the other hand, for certain purposes, such as the manufacture of coloured paints and the compounding of rubber, natural barytes, if ground fairly fine, is not unsuitable. In fact, for use in admixture with coloured pigments, the comparatively coarse natural barytes is to be preferred, as it can be added in larger quantities without unduly destroying the tint due to the coloured substance. Thus an economy of the coloured pigment is effected.[1]

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[1] See M. Toch, "Chemistry and Technology of Paint" (van Nostrand).
[2] W. J. O'Brien, *J. Phys. Chem.* **19** (1915), 113.
[3] Steinau, *Chem. Zeit.* **45** (1921), 741.
[4] S. Stewart, *J. Soc. Chem. Ind.* **39** (1920), 188T.

Barium salts are used in fireworks, and in light-signals, where a green light is required; barium carbonate is used in glass-making, where a glass of high refractive index is demanded.

Barium oxide (BaO) can be made from the carbonate by heating in a gas-fired furnace, a high temperature being needed. When this oxide is heated at 500–600° C. in a current of air, it yields the **peroxide** (BaO_2). Barium peroxide is important as the source of **hydrogen peroxide**; when it is treated with dilute sulphuric acid, barium sulphate is precipitated, whilst peroxide of hydrogen is left in solution.

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[1] T. R. Briggs, *J. Phys. Chem.* 22 (1918), 216.

RADIUM

Atomic weight . 226·0

The last member of Group II$_A$ is of interest on account of its radioactivity rather than its chemical properties. The subject of radioactivity was discussed in Chapter XV (Vol. I) and it is proposed here merely to deal with the chemistry of radium. It must, however, be remembered that the chemical study of radium salts is slightly complicated by the continual production of a radioactive gas, which itself gives rise to other elements (radium A, B, C and D) quite different in chemical properties from radium. When allowance has been made for this fact, the chemistry of radium appears to be very simple, and of no particular interest. Actually radium appears to resemble barium, and is related to the latter in much the same way as barium itself is related to strontium.

The Metal

Metallic radium is seldom prepared, but appears to be very similar to barium, although rather more reactive; it decomposes water with violence. It is best prepared by the amalgam method described in the preparation of strontium.

Compounds

The **salts** of radium are very similar to those of barium, but are on the whole less soluble. The most soluble are the chloride and bromide. Radium **sulphate** is particularly insoluble; its solubility is actually only about $\frac{1}{100}$th of the solubility of barium sulphate.[1] Radium forms a peroxide (RaO_2) besides the ordinary basic oxide, RaO. When introduced into a gas-flame, radium compounds impart to it a carmine tint.

Analytical

Radium is almost invariably detected by radioactive means, the methods having been referred to in Chapter XV, Vol. I. It gives off α-particles, which can be detected and even counted in a suitable instrument by means of the flash which each particle causes when it strikes a screen of zinc sulphide. The amount of radium in a preparation is usually measured by means of an electroscope, the method being based upon the leakage of the charge through air ionized by the presence of the radioactive substance. Radium can be distinguished from the more short-lived radioactive substances (such as radium A, B and C) by the permanent character of its radioactivity.

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[1] S. C. Lind, J. E. Underwood and C. F. Whittemore, *J. Amer. Chem. Soc.* **40** (1918), 435.

The radioactive tests for radium are extraordinarily sensitive, and allow us to recognize and even estimate amounts which could not possibly be detected by any ordinary method of analysis.

TERRESTRIAL OCCURRENCE

Radium occurs in all ores of uranium, being actually produced by the disintegration of uranium atoms. In practically all cases the content of radium in a mineral bears a constant ratio to the content of uranium, namely:—

$$3{\cdot}33 \times 10^{-7} : 1$$

or approximately 1 : 3,000,000.

The ores of uranium (and, therefore, of radium) include the impure oxide

pitchblende, U_3O_8,

a heavy blackish mineral of greasy appearance, which also contains iron, aluminium, lead, barium, and many other metals; this is found in many parts of the world, mainly in pegmatites or metalliferous veins, and notably in Joachimsthal (Bohemia) and in Cornwall. Of more importance, however, is the impure double vanadate

Carnotite, generally expressed as $K_2O.2UO_3.V_2O_5.3H_2O$,

a canary-yellow mineral chiefly found in Colorado and Utah. It occurs there sparsely distributed in sandstone, and has evidently been introduced by the action of infiltrating waters; the uranium has presumably been derived from some primary mineral of the nature of pitchblende. The formula given above does not fully represent the composition, since calcium and often barium is present. It is almost certain that more than one mineral containing vanadium actually occurs in the sandstone.[1] Another source of radium is a complex Australian deposit, known as "Olary ore." This appears to be essentially a titaniferous iron ore, which contains in its crevices a minute amount of carnotite and other uranium minerals, as a yellow incrustation.[2]

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[1] W. F. Hillebrand and F. L. Ransome, *Amer. J. Sci.* **10** (1900), 138–141.

[2] S. Radcliffe, *J. Soc. Chem. Ind.* **33** (1914), 229.

TECHNOLOGY AND USES

Previous to 1898, the Joachimsthal pitchblende was worked as a source of uranium. The residues which contained the radium were thought to be worthless and were dumped on a waste-heap; it was from this waste-heap that Mme. Curie obtained the first preparation of radium salts in 1898. Since then the various uranium ores have been worked mainly for their radium content, although, in the case of carnotite, the vanadium-production is also of great importance.

The greater portion of the world's supply of radium now comes from the American carnotite. Since the actual quantity of radium present in any of the ores is extraordinarily small, the technical extraction is necessarily a laborious process; but experience and patient research have enabled manufacturers to simplify the older processes to a considerable extent, and yet to obtain a high percentage of the radium present in the ores.

The Colorado ores[1] or concentrates are leached with hot concentrated nitric acid, which brings most of the radium and uranium and about half the vanadium into solution, together with much iron, lead and other worthless metals. The bulky residues are separated by filtration. The acid filtrate is nearly neutralized with sodium hydroxide, and mixed with barium chloride, and then with sulphuric acid; barium sulphate is precipitated, and the insoluble sulphates of lead and radium come down with it; the sulphates can then be separated by settling.

From the clear solution that passes off from the settling tanks, iron and aluminium can first be precipitated with boiling sodium carbonate; uranium is next precipitated by means of sodium hydroxide as insoluble sodium uranate, after which the addition of ferrous sulphate to the carefully neutralized solution brings down the vanadium as iron vanadate. The precipitates of sodium uranate and iron vanadate constitute valuable sources of uranium and vanadium respectively.

The treatment of the mixed sulphates of barium, lead and radium must now be considered. The sulphates are converted by heating with charcoal to sulphides, which dissolve readily in hydrochloric acid; the mixture of chlorides is then repeatedly recrystallized from acid solution in silica-lined vessels, until a product comparatively rich in radium is obtained. The lead is removed from the solution of this product by precipitation with hydrogen sulphide in neutral solution, and the radium and barium are precipitated by ammonium carbonate as carbonates, which are then redissolved in hydrobromic acid. Fractional crystallization of the bromides is now carried out, in acid solution, until the product contains a sufficient concentration of radium bromide to be of practical use.[1] Radium almost invariably comes on to the market as a mixture of barium bromide and radium bromide. It has been stated that about 300–500 tons of the ordinary low-grade ore have to be treated to yield one gram of radium in the form of a high-grade salt.

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[1] C. Parsons, R. B. Moore, S. C. Lind and O. C. Schaefer, *U.S. Bur. Mines Bull.* **104** (1915); abstract, *J. Soc. Chem. Ind.* **35** (1916), 44; R.B. Moore, *Bull. Amer. Inst. Min. Eng.* **140** (1918), 1165.

Various modifications of the process have been proposed. Instead of reducing the mixed sulphates with charcoal, they can be reduced by heating with a mixture of calcium hydride and calcium carbide.[2] If, after the treatment, the sulphide produced is treated with normal hydrochloric acid, only the barium and radium sulphides are dissolved; lead sulphide is left unattacked, and lead is thus separated. A convenient way of concentrating the radium in the mixed chlorides is by " fractional precipitation " of the solution by means of hydrogen chloride gas. An alternative method is the fractional adsorption by means of freshly precipitated manganese dioxide (obtained by the interaction of potassium permanganate and manganous chloride in the absence of acid), which adsorbs the radium much more readily than the barium.

The European pitchblendes are treated by methods a little different from those applicable to carnotite.[3] Pitchblende contains, of course, little or no vanadium.

The Australian Olary Ores are treated by a rather different process.[4] The amount of uranium mineral in the ore is very small, and the mineral is therefore crushed, and subjected to magnetic concentration, in which about two-thirds of the worthless iron oxide is removed. The concentrates are insoluble in acids, but can be decomposed by fusion with sodium bisulphate in a reverberatory furnace. The fused product is crushed, and treated with water, a turbid solution being obtained, containing sulphates of iron, uranium, etc., in solution, and sulphates of lead, barium and radium as a fine precipitate. Thanks to the fineness of the precipitate, it passes off in suspension along with the solution when the liquid is drawn off from the heavy residue consisting of the unattacked constituents of the ore. The liquid is run into settling tanks, where the sulphate " slimes " gradually sink to the bottom, about twelve hours being required. The clear liquid can then be drawn off, and the slimes

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[1] A systematic method of fractionation is described by C. E. Scholl, *J. Amer. Chem. Soc.* 42 (1920), 889.

[2] E. Ebler and W. Bender, *Zeitsch. Angew. Chem.* 28 (1915), 25.

[3] R. Sternlicht, *Chem. Zeit.* 38 (1914), 49.

[4] S. Radcliffe, *J. Soc. Chem. Ind.* 33 (1914), 229.

(consisting of sulphates of lead, barium and radium) are worked up for radium.

It is of interest to note that, between the years 1898 (when radium was discovered) and 1920, the quantity of radium extracted in all countries of the world only amounted to 120 grams.[1]

Uses of Radium.[2] The practical importance of radium depends wholly on its radioactivity. It is sometimes asked why radium possesses a greater importance than other radioactive elements. The principal reason is that radium has a period of half-change (1,645 years) long enough to be regarded as a practically permanent source of radioactivity, but, at the same time, short enough to render it a highly active and concentrated source. Furthermore, the fact that it gives off a radioactive gas, which can produce an "active deposit" upon other solid substances, adds considerably to the value of radium for some purposes.

Although, perhaps, radium has not fulfilled all the hopes that were once entertained with regard to it, it has proved a valuable agent in medicine in the treatment of certain forms of cancer, especially where comparatively large quantities have been available. Great efforts are being made to obtain larger quantities of concentrated radium preparations for use at the hospitals. During the war, radium has been applied with success to chronic infected wounds, and has proved effective in the treatment of scars resulting from wounds. It requires to be used with great care since undue exposure to the rays of radium may actually cause cancer instead of curing it.

Another very important use of radium is in the manufacture of luminous paint for application to the hands of watches, and the dials of compasses and other instruments which require to be used in the dark. Ordinary phosphorescent substances, such as zinc sulphide, are luminous in the dark, but only if they have previously been exposed to a fairly bright light. The necessity of making this exposure has proved most inconvenient. If, however, the zinc sulphide is mixed with a minute quantity of a radium salt, which is continually giving out rays which render zinc sulphide luminous, the periodical exposure of the instruments to sunlight becomes unnecessary.

The zinc sulphide requires to be manufactured under special conditions, since some forms are much more active than others; the details of manufacture have not been published. The sulphide, along with the necessary addition of radium, is mixed with an

[1] *J. Röntgen Soc.* **16** (1920), 83.

[2] C. H. Viol and G. D. Kammer, *Trans. Amer. Electrochem. Soc.* **32** (1917), 381.

appropriate "vehicle," and applied to the surface which is to be rendered luminous. It is interesting to note that the paint containing much radium gradually loses its luminosity, since apparently the radium destroys the phosphorescent character of the zinc sulphide. It is thought that luminous paint made according to the British Admiralty Specification loses about half its brightness each year. Paint containing less radium, although less bright when freshly made, would retain its phosphorescent character for a longer period.[1]

Radium has also been advocated as an addition to soils. Several experimenters have claimed that the radium-treatment of soils increases the value of the crops produced, but it seems highly improbable that such treatment would prove remunerative.[2]

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[1] F. H. Glew, *Chem. Drug.* 88 (1916), 653.

[2] See *U.S. Dept. Agr., Bureau of Soils, Bull.* 149 (1914).

GROUP IIIA

	Atomic Weight.
Boron	10·9
Aluminium	27·1
Scandium	45·1
Yttrium	89·33
Lanthanum	139·0
Actinium	232·0

The elements of Group IIIA are far less basic in character than those of Group IIA. The first member of the group, boron, is usually accounted a non-metal, and will be discussed only briefly in this volume; its oxide is weakly acidic in character, and can only display basic properties towards a few strong acids.

Aluminium is typically metallic in its physical characters, but the oxide, although essentially a weak base, has also still more feebly developed acidic properties.

The next three metals of the group, scandium, yttrium and lanthanum, are basic in character, but much less strongly basic than the metals of Group IIA; these three elements so closely resemble that unique cluster of elements known as the "rare earth metals," which follow lanthanum in the order of atomic weights, that they will be regarded as members of the rare earth group. Actinium, which possesses interest as a radioactive substance, has also chemical properties very similar to those of the rare earth elements.

In passing from Group IIA to Group IIIA, we note, along with the loss of marked basic properties, an increased tendency to form highly insoluble compounds. The hydroxides, for instance, are extremely insoluble, as is indicated by the gelatinous form in which they are commonly precipitated.

The elements are in all cases trivalent, and the compounds, for the most part, colourless.

BORON

Atomic weight . . 10·9

The Element

Boron is usually considered as a non-metal, and requires only a brief mention in this volume. It resembles the element carbon—which follows it in the order of atomic numbers—much more closely than it resembles any element of its own group.

The element is usually met with as a chestnut-brown or black amorphous powder, which may be compared to the ordinary amorphous form of carbon. When crystallized from molten aluminium it is obtained in the form of very hard transparent yellowish crystals, which may aptly be compared with the diamond.

Boron does not conduct electricity and has none of the physical properties of a metal. It is an exceptionally light element, the specific gravity being only 2·5. It is appreciably volatile at the temperature of the electric arc, but appears to vaporize without melting.[1]

Powdered boron burns when heated in air, yielding the oxide, sometimes mixed with the nitride. The element appears fairly stable at low temperatures. It does not cause the evolution of hydrogen from mineral acids (e.g. hydrochloric), but is oxidized by nitric or concentrated sulphuric acid, with the formation of boric acid.

When introduced into the solution of a salt of silver, gold or platinum, boron causes the precipitation of the metal in the elementary condition.

Laboratory Preparation. The element is best obtained by heating the trioxide with magnesium powder in a crucible, the trioxide being in excess, so as to hinder the formation of magnesium boride. The button obtained on cooling is broken up and the central portion, which has a brown colour, is separated and boiled, first with water so as to remove excess of oxide, and then six times with dilute hydrochloric acid, and finally with hydrofluoric acid, so as to dissolve out the magnesium boride and borate that are present in the mass. Finally the residue of amorphous boron is washed with water and dried.[2] The product of this process invariably contains magnesium, and, although this can partly be eliminated by subsequent heating with boron trioxide, the boron obtained is never quite pure.

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[1] H. Moissan, *Comptes Rend.* **117** (1893), 424.

[2] H. Moissan, *Comptes Rend.* **114** (1892), 392.

Recent work has shown that it is possible to obtain boron in a state of high purity by the action of a high-tension arc upon the vapour of boron bromide. Dissociation of the bromide into boron and bromine occurs, and if freshly reduced copper is introduced into the vessel, the bromine may be removed as quickly as it is formed. This method is capable of yielding boron of 99·8 per cent. purity, but, as a pressure of 80,000 volts is needed, it could not be carried out in every laboratory.[1]

Compounds

Boron is trivalent in all its compounds. The **trioxide,** B_2O_3, is formed when boron is heated in oxygen, or when the hydrate, boric acid, is heated to redness. When the fused oxide is cooled down, there is a marked tendency to form a glass, instead of crystallizing—a tendency characteristic also of the borates. The oxide is a white non-volatile solid. On account of the non-volatility, boron oxide is capable of expelling other oxides from combination with a base. For instance, sodium sulphate strongly heated with boron trioxide, yields sodium borate ; sulphur trioxide—although an oxide of far more pronounced acidic properties—is driven off as vapour.

Boron trioxide is soluble in water, and from the solution, **boric acid,** H_3BO_3 or $B(OH)_3$, may be obtained by crystallization in shining colourless scales. Dry boric acid, when in the powdered condition, produces a curious "soapy" sensation when rubbed between the fingers.

In spite of the non-volatility of the anhydride (B_2O_3), boric acid itself is very appreciably volatile in steam. When a solution of boric acid is evaporated, it loses, at first, water vapour alone, but, as the solution becomes concentrated, boric acid commences to distil away along with the steam.[2] Boric acid is also extremely volatile in the vapour of methyl or ethyl alcohol. This is probably due to the formation of an ester with low boiling-point ; methyl borate, for instance, boils as low as 65° C.

A solution of boric acid shows only very feeble acidic properties. It turns a solution of blue litmus purple-red, but does not give the true red produced by stronger acids ; methyl orange is unaffected by boric acid. The hydrion concentration appears to be increased by the presence of glycerine or mannitol, possibly owing to the formation of some strong complex acid. At any rate, in the presence of glycerine, boric acid is able to discharge the pink colour of alkaline phenol-phthalein.

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[1] F. Meyer and R. Zappner, *Ber.* **54** (1921), 550.

[2] L. de Koningh, *J. Amer. Chem. Soc.* **19** (1897), 385.

Boric acid combines with bases yielding borates. The most important of these is sodium pyroborate (*borax*), $Na_2B_4O_7.10H_2O$ or $Na_2O.2B_2O_3.10H_2O$, which crystallizes in colourless monoclinic prisms from a solution of boric acid to which sodium carbonate has been added. Solutions of borax are strongly alkaline, owing to hydrolysis.

When hydrated borax is heated, it gives off water, swelling up in a most striking manner, and finally subsiding into a mass of molten anhydrous borax. When cooled down, the anhydrous borax does not easily crystallize, but forms a glass; the glass devitrifies on keeping. Molten borax dissolves several metallic oxides, which impart characteristic colours to it; hence the use of borax in qualitative analysis.

Many borates (notably those of calcium, barium, lead and silver) are practically insoluble, and are prepared by the ordinary method of precipitation.

The **perborates** can be produced by the action of hydrogen peroxide on the solutions of the borates; of these sodium perborate, $NaBO_3.4H_2O$, is the best known. They have mild oxidizing properties and liberate iodine from potassium iodide.

Although boron trioxide is essentially acidic in its properties, it does appear to form unstable compounds with sulphuric acid or sulphur trioxide; and, although these are not usually styled "sulphates" in the textbooks, their formation may perhaps be taken to indicate that the oxide does possess feebly developed basic properties.[1] For instance, on the addition of powdered boric acid to a large quantity of sulphur trioxide, a violent reaction occurs, and the whole mixture liquefies. If the excess of sulphur trioxide is driven off by heating at 100° C., a solid separates on cooling, which, when dried in a desiccator, has the composition $B(HSO_4)_3$.

Boron forms very interesting volatile compounds with the halogen elements. The **chloride**, BCl_3, can be obtained by the action of chlorine on boron, but is more conveniently prepared by passing a stream of chlorine gas over a strongly heated mixture of boron trioxide and carbon, the vapour being condensed in a U-tube placed in a freezing mixture. It is a colourless liquid, boiling at as low a temperature as 18° C. It is thus difficult to preserve. When introduced into water, it is hydrolysed to boric and hydrochloric acids.

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[1] R. F. D'Arcy, *Trans. Chem. Soc.* **55** (1889), 155.

The **fluoride,**[1] BF_3, is even more volatile, being at ordinary temperatures a gas having a very unpleasant odour; it liquefies at − 101° C. and solidifies at − 127° C. It can be produced by the direct action of fluorine on boron, but there are various alternative methods of preparation.

Like the metals of the previous group, boron has an affinity both for hydrogen and nitrogen. Various **hydrides**[2] are known. A mixture of hydrides can be obtained in the following way. Boron oxide is heated with excess of magnesium, and the product, which contains magnesium boride, is treated with acid in a vessel through which a slow stream of hydrogen is passed. The gas leaving the vessel, consisting of hydrogen mixed with the vapour of boron hydrides, is passed through drying-tubes containing calcium chloride and phosphorus pentoxide, and then through a tube cooled in liquid air, in which a mixture of boron hydrides, together with traces of silicon hydride and carbon dioxide, condense in the solid state. By fractional distillation of the snow-like product two hydrides of boron can be isolated. The composition and vapour density of these two hydrides correspond to the formulæ B_4H_{10} and B_6H_{12} respectively; both are liquid at ordinary temperatures. Various other hydrides are known. When B_4H_{10} is heated, it yields a gaseous hydride B_2H_6 along with a solid hydride $B_{10}H_{14}$, and other products. It is stated that probably at least ten hydrides of boron exist. The volatile hydrides have disagreeable odours and are very poisonous.

The **nitride,** BN, can be formed by the action of nitrogen on boron at very high temperatures, or, more conveniently, by passing ammonia over boron trioxide mixed with calcium phosphate, which serves to render the mass porous and thus to give the ammonia access to the boron trioxide.[3] Another method of preparation, which is said to give a purer product, depends on the action of ammonia on boron chloride.[4] Boron nitride is a colourless solid, insoluble in cold water, but decomposed by boiling water, yielding ammonia and boric acid.

Analytical

Any volatile compound of boron confers a green colour on a flame. This fact can be used in the detection of a borate. The substance in which the presence of a borate is suspected should be mixed with calcium fluoride and potassium disulphate (free from boron); a little of the mixture, slightly moistened, is then held on the end of a clean platinum wire, and the reducing flame of the blowpipe is directed on the mixture. A green coloration, best seen against a black background, indicates boron.[1] The object of the calcium fluoride is to convert the boron to the volatile boron fluoride, BF_3.

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[1] H. Moissan, *Comptes Rend.* **139** (1904), 711.

[2] A. Stock and C. Massenez, *Ber.* **45** (1912), 3539; A. Stock and K. Friederici, *Ber.* **46** (1913), 1959; A. Stock, K. Friederici and O. Priess, *Ber.* **46** (1913), 3353; A. Stock, *Zeitsch. Elektrochem.* **19** (1913), 779.

[3] L. Moeser and W. Eidmann, *Ber.* **35** (1902), 535.

[4] F. Meyer and R. Zappner, *Ber.* **54** (1921), 560.

Small traces of boric acid are also detected by means of the vegetable colouring matter turmeric. The substance to be examined is dissolved in dilute hydrochloric acid, and a few drops of the solution applied to yellow turmeric paper. If boric acid is present, the paper turns reddish-brown on drying, and changes to blue-black, grey or green on the addition of dilute alkali. A quantitative method for the colorimetric estimation of boric acid based on the reaction with turmeric solution has been worked out.[2] It should be noticed, however, that zirconic, titanic, tantalic, niobic and molybdic acids produce a rather similar change with turmeric.[3]

The precipitation methods devised for the separation of boron are not easy, but various processes have been devised depending on the fact that boric acid is volatile in a current of methyl alcohol.[4]

Boric acid can be titrated with sodium hydroxide in the presence of glycerine, phenol-phthalein being employed as indicator. Any stronger acids present in the solution should first be neutralized; for this preliminary neutralization, methyl orange or para-nitrophenol, indicators which are unaffected by boric acid, are useful. Having obtained neutrality towards methyl orange, glycerine is added and a few drops of phenol-phthalein; then sodium hydroxide is run in until a pink colour appears. From the amount of sodium hydroxide needed, the quantity of boric acid present may be calculated according to equation,

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O.$$

TERRESTRIAL OCCURRENCE

Being a comparatively rare element, the boron contained in igneous intrusions collects in the last solidifying portion of the mass. Since many of the compounds of boron are distinctly volatile, it is largely expelled in the vaporous state, along with the other elements, such as fluorine, tin, lithium and beryllium, which also have volatile compounds. Many of these vapours act chemically upon the rocks through which they pass, and, in this way, various boron-containing minerals are produced. For instance, tourmaline, a complex borosilicate of aluminium and other metals, is produced where the vapours have passed through granitic rocks. It is of interest to prospectors not only on account of its own value (some varieties are attractive gem-stones), but also because it is frequently associated with other valuable minerals, notably tin-stone.

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[1] Sir W. Crookes, "Select Methods in Chemical Analysis," (Longmans).

[2] See V. Samter, "Analytische Schellmethoden" (Knapp).

[3] F. P. Treadwell, "Analytical Chemistry"; translation by W. T. Hall, 1911 edition, page 67 (Chapman & Hall).

[4] F. A. Gooch and L. C. Jones, *Zeitsch. Anorg. Chem.* **19** (1899), 417. Working details given by W. W. Scott, "Standard Methods of Chemical Analysis" (Crosby Lockwood). See also O. von Spindler, *Chem. Zeit.* **29** (1905), 582.

Whilst, however, a good deal of the boron in the vapours and hot waters given off by igneous masses is lost by reaction with rocks, a certain amount reaches the surface of the earth. In the volcanic regions of Tuscany, some of the jets of natural steam that arise from the ground contain an appreciable amount of boric acid (which, as has been stated, is quite volatile in steam). Hot springs containing borates occur in the volcanic district of the Yellowstone Park. In such a way boron compounds have come to exist in terrestrial waters, and, although there are only very small amounts in the ocean, certain inland lakes, notably the great Borax Lake of North California, contain a great deal of sodium borate; in that particular case, the supply almost certainly came from hot springs in the neighbourhood.

By the natural evaporation of such lakes, deposits of solid salts —including borates—are formed. Evidently the crusts of boron minerals found in the marshes of South California have been formed in this way. The salts contain not only

Borax . . . . $Na_2B_4O_7.10H_2O$

but also calcium borates such as

Colemanite . . . . $Ca_2B_6O_{11}.5H_2O$.

Important deposits occur in Chili, in the same desert regions where the nitrates are found. Here the main mineral is a double borate,

Ulexite . . . . . $NaCaB_5O_9.8H_2O$.

A third important borate-producing district is the region of Panderma, on the Sea of Marmora, where calcium borate[1] occurs under the name of

Pandermite . . . . $Ca_2B_6O_{11}.3H_2O$.

In addition, deposits of crude borax occur in Thibet.

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[1] Some authorities speak of the mineral coming from this district as a magnesium borate, but the principal metal—at any rate in the mineral now sent to this country—is calcium.

It is interesting to note that borates—evidently produced by the gradual concentration of the small quantity present in the sea—occur in the salt deposits of Stassfurt. But the minerals there occurring, such as

Boracite . . . . $2Mg_3B_8O_{15}.MgCl_2$,

are mainly borates of magnesium, not of calcium.

Technology and Uses

The borate deposits of California, Chili and Asia Minor now form the most important sources of boron compounds. Where soluble sodium borate is still found, it may only require recrystallization to yield the salt in a sufficient state of purity. But generally speaking the deposits consist mainly of calcium borates, which require decomposition in order to give the commercially useful compounds of boron.

Essentially the process is a double decomposition. The minerals are ground, and boiled with a solution containing sodium carbonate and bicarbonate. Calcium carbonate is precipitated, and can be removed by filter-pressing whilst hot; the filtrate is run into big tanks, where the borax separates on cooling in aggregates of large glittering crystals.

Where it is desired to prepare boric acid, the method is modified, the ground mineral being decomposed with acid. If hot hydrochloric acid is used, boric acid separates from the solution on cooling in shining lamellæ; the highly soluble calcium chloride remains in solution. If sulphuric acid is used, the precipitate of calcium sulphate is separated by filtration whilst hot, and the boric acid crystallizes from the filtrate. In either case, the boric acid is purified by recrystallization. Some care must be taken in the manufacture of boric acid to avoid loss due to the volatility of the acid in steam.

A considerable amount of boric acid is still obtained from the hot springs of Italy.

Boric acid is employed largely as a preservative in foodstuffs, and is used as a mild antiseptic.

Anhydrous borax is used in the glass industry; glasses containing borates have usually low softening-points; for the same reason, borax and boracic acid is useful in the manufacture of enamels and glazes. Owing to its capacity for dissolving metallic oxides, borax is used as a flux in metallurgy, and also in brazing and soldering. Borax is also added to soap mixtures intended for use in hard water. The borates of manganese and lead are used as "driers" for oils. Several of the perborates have also a technical importance.

Sodium perborate, $NaBO_3.4H_2O$, made by the action of sodium peroxide on boric acid, is used for bleaching; it is less destructive to the materials than many of the more violent oxidizing agents.

A good deal of sodium perborate is also prepared electrolytically, especially in Germany.[1] A solution containing borax and sodium carbonate is believed to be used; perborates are formed at the anode, and after electrolysis, the solid sodium perborate can be separated by a slight cooling. The factors governing the efficient production of borates are the same as those discussed in connection with the electrolytic preparation of chlorates and hypochlorites; perborates are formed (directly or indirectly) at the anode, but, if they come in contact with the cathode surface, they are liable to be destroyed. Substances like the chromates and turkey red oil, which form films over the cathode surface, decrease the loss due to this cause. Very pure chemicals are needed for the manufacture of perborates. The presence of iron, for instance, catalytically accelerates the cathodic destruction of the product. Tin may be used as a cathode-material; but the only suitable anode material is platinum—a fact that naturally adds to the cost of the electrolytic process.[2]

Owing to its affinity for oxygen, boron is sometimes added as a deoxidizer to metals, notably copper, aluminium, nickel and their alloys, before casting; it is introduced into the molten metal, in the form of the so-called "*suboxide*," a product made by the action of magnesium on excess of boron trioxide. The "suboxide" is probably boron containing the trioxide in solid solution. Experiments have shown that boron can also be employed, with advantage, in steel, being in this case added as an iron-boron alloy ("ferro-boron").

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[1] K. Arndt, *Chem. Zeit.* **39** (1915), 806; K. Arndt and E. Hantge, *Zeitsch. Elektrochem.* **28** (1922), 263. See also P. C. Alsgaard, *J. Phys. Chem.* **26** (1922), 137.

[2] K. Arndt, *Elektrotech. Zeitsch.* **42** (1921), 345.

ALUMINIUM

Atomic weight 27·1

The Metal

Aluminium is a white metal, which assumes a bright lustre when polished. It is one of the lightest metals known, the specific gravity being about 2·70; the specific gravity varies slightly according as the metal is in the cast, rolled or annealed condition.[1] Although, considerably harder than most of the metals so far considered, aluminium is both ductile and malleable; both wire and thin leaf can be obtained without difficulty. The crystalline form is cubic, the atoms being arranged—according to the result of X-ray analysis —on a face-centred lattice.[2]

Cast aluminium when viewed in a micro-section shows the ordinary granular structure of cast metals, but when subjected to mechanical deformation, the structure becomes modified. When cast aluminium is gradually rolled out into thin sheets above 400° C., the individual crystals become greatly elongated in the direction of rolling, and flattened in the direction at right angles.[3] It has sometimes been stated [4] that excessive cold-work renders the metal structureless, converting the crystalline metal almost entirely into amorphous material; it seems likely, however, that much crystalline aluminium always remains, although possibly in some cases it may be difficult to detect the crystalline structure in micro-sections. Nevertheless sufficient "amorphization" occurs during deformation to cause a considerable increase in hardness and ductility; the amorphous or pseudo-amorphous material is probably formed mainly at the boundaries of the distorted crystal-grains. Annealing renders the work-hardened metal soft and ductile again. At high temperatures (500–600° C.) the softening is quite rapid; at lower temperatures (100–300° C.) it requires many hours. The loss of the acquired hardness and strength on annealing is, however, not always accompanied by the complete recovery of ductility—as judged by the elongation test.[5]

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[1] F. J. Brislee, *Trans. Faraday Soc.* **9** (1913), 162.

[2] A. W. Hull, *Phys. Rev.* **10** (1917), 661.

[3] H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* **25** (1921), 259.

[4] F. J. Brislee, *Trans. Faraday Soc.* **12** (1916–17), 57. Compare R. J. Anderson, *J. Franklin Inst.* **187** (1919), 1.

[5] H. C. H. Carpenter and L. Taverner, *J. Inst. Met.* **18** (1917), 115.

The exceptional weakness which is sometimes met with in aluminium which has first been hardened by deformation and then annealed is, in some cases at least, due to the presence of very large crystals. As usual, the formation of large crystals is most likely to occur when the degree of deformation has been small. Highly deformed aluminium acquires on annealing a comparatively fine-grained structure, and it appears that recrystallization, in this case, always starts from nuclei which arise spontaneously at the boundaries of the deformed crystals.[1] If we imagine that "amorphous" material is produced, during the deformation, at the crystal-boundaries, the initiation of crystallization at these points need occasion no surprise.[2]

By very mild deformation of a bar of ordinary fine-grained aluminium, followed by suitable heat-treatment, Carpenter and Elam[3] have succeeded in converting the whole bar into a single crystal, the orientation of the atoms being thus rendered uniform throughout all parts of the specimen. To obtain this remarkable result, they gently pulled a number of bars in an ordinary machine until the extension of each bar was about 2 per cent. of the original length. The bars were then placed in a furnace at 450° C., and the temperature was gradually raised (by 15–20° C. per day) until it reached 550° C.; finally the bars were heated at 600° C. In each bar at some moment during the gradual heating, some one crystal-grain which happened to be favourably situated would commence to grow at the expense of its neighbours, and would continue to grow until it extended over the whole bar. Sometimes a second grain—or perhaps two or three others—might commence to grow before the first had developed over the whole bar, and in such cases the bars in the final state would consist of two, three or four crystals; but if the heating was sufficiently slow, this could often be avoided, and a considerable proportion of the bars treated were found—after cooling—to consist of single crystals. A study of the behaviour of these single-crystal specimens to a tensile stress is of the greatest interest, and has greatly extended our knowledge of the mechanism of gliding and twinning. In general the single-crystal specimens show a much smaller tensile strength than similar specimens consisting of numerous small grains, but the tensile strength of different single-crystal specimens varies considerably; this is actually to be expected, since the orientation of the rows of atoms will be different in different specimens, and it is quite in accordance with our knowledge of crystals that their strength should be different when they are tested in different directions.

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[1] H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* **24** (1920), 83; **25** (1917), 259.

[2] U. R. Evans, *J. Inst. Met.* **25** (1921), 298.

[3] H. C. H. Carpenter and C. F. Elam, *Proc. Roy. Soc.* **100** [A] (1921), 329.

The **chemical behaviour** of metallic aluminium is somewhat anomalous. It is in some respects one of the most reactive metals commonly met with; at high temperatures it oxidizes rapidly in air, whilst aluminium powder reduces the oxides of the less reactive metals to the elemental condition, great heat being evolved during the change. Nevertheless compact aluminium remains unchanged in the air at ordinary temperatures, and keeps its brightness far better than lead and copper, for instance.

This is, without doubt, due to a thin skin of colourless, transparent oxide which is normally closely adherent and acts like a "plating" of a noble material upon aluminium. The oxide-film produced upon aluminium at ordinary temperatures is too thin to be visible; but when thin aluminium foil is heated at 800° C., the foil, although still unchanged in appearance as viewed by reflected light, becomes quite transparent when viewed by transmitted light, and may be seen to consist mainly of oxide containing numerous beads of unchanged metal. By the action of hot strong nitric acid, the unchanged metal can be removed, leaving the oxide as a mass of colourless iridescent scales.[1]

The close adhesion of the oxide-film naturally depends as much on the character of the underlying metal as on that of the oxide, and it is not surprising to find that a small change in the surface may alter the adhesion, and hence the rate of attack by the air. If aluminium is rubbed with mercury and then exposed to the air, it oxidizes very rapidly; evidently the oxide formed does not adhere well to the amalgamated surface, and therefore produces no protective film which would prevent further action.[2]

Although ordinary compact aluminium is but little affected by exposure to the air, aluminium powder—owing to its large surface area—oxidizes more readily, especially when heated. At 600° C. only the oxide is produced, but at high temperatures (800–1,000° C.) the product contains nitride also.[3]

The existence of the oxide film also explains the comparative slowness with which compact aluminium enters into reactions with aqueous solutions. For instance, aluminium placed in a solution of copper sulphate, does not readily cause a separation of metallic copper. The behaviour of the metal towards reagents in general depends largely on their power to dissolve or loosen the oxide film.

[1] R. Seligman and P. Williams, *J. Inst. Met.* **23** (1920), 169.

[2] L. Kahlenberg and J. A. Montgomery, *Trans. Amer. Electrochem. Soc.* **36** (1919), 285–288. See also R. Müller and F. Hölzl, *Zeitsch. Anorg. Chem.* **121** (1922), 103; especially pages 108, 109.

[3] E. Kohn-Abrest, *Comptes Rend.* **150** (1910), 918.

Aluminium evolves hydrogen readily from solutions of caustic alkali, aluminates being produced in the solution. Hydrochloric acid also acts on aluminium causing a fairly brisk evolution of hydrogen; sulphuric acid acts much less readily.[1] Very concentrated nitric acid scarcely acts on aluminium at all, but the dilute acid attacks it to an appreciable extent, especially if the temperature is raised, or if oxides of nitrogen are present[2]; it should be noted that the rate of attack by nitric acid depends also on the mechanical condition of the metal—whether cold-worked, partially annealed or thoroughly annealed.[3]

The action of organic acids has been studied by Seligman and Williams, who have obtained results of great interest.[4] One per cent. acetic acid was found to attack aluminium fairly readily, but, as the concentration of the acid tested increased, the rate of corrosion decreased. Ninety-nine per cent. acetic acid was practically without action, and one would expect that absolutely anhydrous acid would likewise prove to be inactive. But, as a matter of fact, it was found that the removal of the last 0·05 per cent. of water from the acid increased the rate of attack one-hundredfold. Similar results were obtained with palmitic and oleic acids, and also with phenol and even alcohol. The power of a mere trace of water to inhibit the action is certainly remarkable; it has been explained on the supposition that—in the presence of water—the soluble organic salt is hydrolysed, producing hydroxide, or a basic salt, which adheres to, and protects, the metal.

The action of salt solutions upon aluminium has also been studied in detail. The metal is attacked by solutions of many salts (especially by chlorides), hydrogen being evolved; as a rule, however, the rate of corrosion, which at first increases with the time, decreases again, evidently owing to the formation of an obstructive coating of aluminium hydroxide.[5] As in so many cases, chlorides tend to loosen the film and make it less perfectly protective.

The anodic behaviour of aluminium has already been discussed in Chapter XII (Vol. I). It is only necessary to repeat here that valve action is shown towards most solutions. In other words, aluminium will not function as an anode at low E.M.F.s; in a solution of ammonium borate an E.M.F. as high as 500 volts must be applied before the insulating film breaks down. If, however, the solution contains chlorides, a considerable leakage of current takes place at the surface of an aluminium anode even at quite low E.M.F.s. The rectifying effect of the aluminium electrode is directly due to the presence of a film of oxygen upon the surface of an anodically polarized aluminium electrode; this gas-film can be crossed by electrons in one direction but not in the other. The gas-film would, however, never come to be produced if the aluminium were not covered, at the moment of immersion in the electrolyte, with a protective oxide-film, which prevents the passage of aluminium into the ionic condition.

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[1] See W. D. Richardson, *Trans. Amer. Electrochem. Soc.* 38 (1920), 265, 267.

[2] R. Seligman and P. Williams, *J. Soc. Chem. Ind.* **35** (1916), 665.

[3] R. Seligman and P. Williams, *Trans. Faraday Soc.* **12** (1916–17), 64.

[4] R. Seligman and P. Williams, *J. Soc. Chem. Ind.* **35** (1916), 88; **37** (1918), 159T.

[5] G. H. Bailey, *J. Soc. Chem. Ind.* **39** (1920), 118T.

Laboratory Preparation. Although aluminium does not, in practice, readily pass into aqueous solution, it stands too near the negative end of the Potential Series to be deposited from an aqueous solution of its salts by electrolysis under ordinary conditions. When an aluminium salt solution is electrolysed, hydrogen alone is produced at the cathode. It is very difficult to make the cathodic potential so negative that aluminium deposition could begin, although certain experimenters—using a very high current density and a rotating cathode—have succeeded in showing that the deposition of aluminium from an aqueous solution is possible.[1] It will never, however, be a convenient method of preparing the metal.

The metal can be produced in the laboratory by the electrolysis of a fused bath, for instance sodium aluminium fluoride containing dissolved alumina, the process being founded on that used on a commercial scale.[2] Or it can be obtained by the action of a still more reactive metal, like sodium, upon the fused fluoride, or upon sodium aluminium chloride. It is rarely prepared in the laboratory, and the description of the technical metallurgy must be reserved for the technological section.

An interesting method of preparing very pure aluminium from the commercial metal has recently been published.[3] It depends on the fact that when molten impure aluminium solidifies, the crystals are comparatively pure in the early stages of growth; the main impurities, iron and silicon, remain liquid until the last moment, when they separate as a eutectic. If technical aluminium is allowed to crystallize slowly, and is stirred vigorously during the solidification, a spongy aggregate of crystal grains is obtained, which can afterwards be broken up into a coarse powder; each grain consists of a core of fairly pure aluminium surrounded by a thin layer of eutectic containing the impurities. The granular mass is then extracted with 1 per cent. hydrochloric acid, which dissolves off most of the impure film, leaving the purer metal below untouched. When the extraction with fresh hydrochloric acid ceases perceptibly to dissolve away iron, the granules are washed with water and then remelted, the whole purification being repeated until the necessary purity is obtained.

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[1] S. A. Tucker and E. G. Thomssen, *Trans. Amer. Electrochem. Soc.* 15 (1909), 497; A. H. Cowles, *Trans. Amer. Electrochem. Soc.* 15 (1909), 503.

[2] S. A. Tucker, *Electrochem. Ind.* 7 (1909), 315.

[3] F. and W. Mylius, *Zeitsch. Anorg. Chem.* 114 (1920), 27.

Compounds

Aluminium is trivalent in all its compounds. The salts are colourless substances, except where derived from coloured acids.

Aluminium oxide (*Alumina*), Al_2O_3, is obtained when aluminium powder is heated in air. Like the oxides of calcium and magnesium, it is extremely infusible. Only the oxy-hydrogen blowpipe or the electric furnace can melt it. When obtained at a high temperature, the oxide is compact, crystalline, very hard and almost insoluble in acids. The hard naturally-occurring form of alumina (corundum) is also practically undissolved by acids, and evidently has been produced at a high temperature. When obtained, however, by igniting the hydroxide at a low temperature, alumina is dissolved by acids and also by alkalis at an appreciable rate. In this respect, alumina resembles beryllium oxide.

The porous alumina obtained by heating the hydroxide at 275° C. is quite hygroscopic, and takes up a considerable amount of water when exposed to damp air at the ordinary temperature. But this appears to be due merely to adsorption, and not to the regeneration of the hydroxide.[1]

The corresponding **hydroxide**, usually written $Al(OH)_3$, is obtained when a hot solution of an aluminium salt is precipitated with ammonia. It is a white gelatinous precipitate, which naturally, when separated on a filter, contains more water than corresponds to the formula $Al(OH)_3$. By studying the expansion of an aluminium hydroxide gel on freezing, it is possible to distinguish between the combined water, and the water contained in the pores of the gel or adhering to the surface of the mass; researches based on this principle appear to show that the composition of the hydroxide corresponds approximately to the formula $Al(OH)_3$, but that the substance contains a small excess of water in solid solution.[2] When treated with dilute sodium hydroxide, the gelatinous precipitate is slowly converted to a crystalline variety, in which bar-shaped crystals are distinctly visible under the microscope.[3] The crystalline form, dried at 100° C., has the composition $Al_2O_3.3H_2O$ or $Al(OH)_3$.

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[1] L. H. Milligan, *J. Phys. Chem.* **26** (1922), 247.

[2] H. W. Foote and B. Saxton, *J. Amer. Chem. Soc.* **38** (1916), 588; **39** (1917), 1103.

[3] F. Goudriaan, *Proc. Amst. Acad.* **23** (1920), 129; *Rec. Trav. Chim.* **41** (1922), 82.

The hydroxide dissolves in acids, yielding aluminium salts, and also in alkalis giving aluminates. Solutions of aluminates, however, hydrolyse readily, the hydroxide being sometimes deposited spontaneously, especially if the solution is exposed to air containing carbon dioxide. The hydroxide prepared by the slow decomposition of an aluminate solution is quite different in appearance from that prepared by precipitation of an aluminium salt with ammonia, being dense and granular, instead of gelatinous. When dried at 100° C., it has the composition $Al_2O_3.3H_2O$ or $Al(OH)_3$, and, unlike the dried gel, is not hygroscopic.[1] When heated it loses part of the combined water at 225–235° C., but dehydration is only complete at about 1,000° C.

The gelatinous form of aluminium hydroxide readily undergoes "peptization," colloidal solutions being produced. Dilute acetic acid, for instance, appears to dissolve it, yielding a liquid containing colloidal particles visible under the ultra-microscope ; this solution is flocculated by the addition of hydrochloric acid. Concentrated acetic acid, however, dissolves aluminium hydroxide, giving a true solution of the acetate.[2] Aluminium salts also act as peptizing agents ; a colloidal solution is obtained by the action of aluminium chloride on the gelatinous hydroxide.[3] The peptization is apparently due to preferential adsorption of aluminium ions, for the colloid particles are found to carry a positive charge. When washed quite free from precipitating electrolytes by means of a centrifuge, aluminium hydroxide is capable of being peptized by pure water.[4]

Like beryllium hydroxide, aluminium hydroxide is quite quickly dissolved by mineral acids when fresh ; but, if kept for some time, and especially if boiled with water, it becomes denser and less reactive. The diminished reactivity is due to the agglomeration of the original particles, and the consequent diminution of the active surface.

Aluminium salts are formed by dissolving the hydroxide, or the metal, in the acid required. The **sulphate**, $Al_2(SO_4)_3$, is very soluble and forms several hydrates. When a solution containing potassium sulphate is evaporated and allowed to cool, a double salt, "**potash alum**," $K_2SO_4.Al_2(SO_4)_3.24H_2O$, which is much less soluble, crystallizes out in regular octahedra. This is a member of a large group of isomorphous bodies, all of which crystallize in the cubic system. Thus, if a solution containing ammonium and aluminium sulphates is crystallized, ammonia alum is obtained. Most monovalent elements can replace the potassium, and, on the other hand, a large number of other trivalent metals can replace the aluminium. Examples of a few typical alums are given below:—

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[1] E. Martin, *Mon. Scient.* **82** (1915), 225. See also F. Goudriaan, *Proc. Amst. Acad.* **23** (1920), 129.

[2] W. B. Bentley and R. P. Rose, *J. Amer. Chem. Soc.* **35** (1913), 1490.

[3] H. B. Weiser, *J. Phys. Chem.* **24** (1920), 505.

[4] R. Bradfield, *J. Amer. Chem. Soc.* **44** (1922), 965.

Potash alum	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Ammonia alum	$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$
Cæsium alum	$Cs_2SO_4.Al_2(SO_4)_3.24H_2O$
Silver alum	$Ag_2SO_4.Al_2(SO_4)_3.24H_2O$
Thallium alum	$Th_2SO_4.Al_2(SO_4)_3.24H_2O$
Chrome alum	$K_2SO_4.Cr_2(SO_4)_3.24H_2O$
Iron alum	$K_2SO_4.Fe_2(SO_4)_3.24H_2O$

All these substances crystallize in octahedra. One alum may be deposited upon crystals of another; for instance, an octahedral crystal of a colourless alum containing aluminium, if placed in a supersaturated solution of chrome alum, will become covered with a layer of purple chrome alum in crystalline continuity with the colourless aluminium alum below.

Aluminium **nitrate** is soluble and somewhat deliquescent. The anhydrous **chloride,** which is, like the chlorides of calcium and magnesium, extremely hygroscopic, is difficult to obtain from the solution; when evaporated to dryness, the solution loses hydrogen chloride, the oxide being left. Aluminium chloride can be made by passing chlorine over aluminium, or over aluminium oxide intimately mixed with carbon and heated in a hard-glass tube. It is quite volatile, subliming about 190° C. The vapour density above 750° C. indicates that the simple molecules $AlCl_3$ are present. At lower temperatures—at which many chlorides would be solid—association to Al_2Cl_6 seems to occur. But this fact does not compel us to conclude that Al_2Cl_6 is a more correct formula than $AlCl_3$ for the chloride in the solid and the dissolved state—as many chemists still seem to suppose.

Solutions of aluminium salts of powerful acids react acid to indicators, indicating that hydrolysis occurs in the solution. This shows that aluminium hydroxide is a much more feeble base than the hydroxides of the metals of the previous groups. When the chloride or acetate solutions are evaporated, alumina can be obtained; the oxide is also produced by heating the anhydrous sulphate.

The **fluoride,** AlF_3, is obtained when the metal is dissolved in hydrofluoric acid. By evaporation of the solution, and distillation of the residue in a current of hydrogen, aluminium fluoride sublimes without decomposition; the transparent crystals collecting in the receiver are found scarcely to dissolve in water. Various double fluorides are known; the sodium aluminium fluoride, $3NaF.AlF_3$, occurs in nature as the mineral **cryolite.**

The **sulphide,** Al_2S_3, is best formed when aluminium is heated with sulphur. Being the salt of a weak acid and a weak base, hydrolysis is to be expected when it is treated with water. In actual fact, it is found to be decomposed at once when water is dropped on to it, hydrogen sulphide gas being evolved. Aluminium sulphide has been proposed as a suitable material from which the gas can be generated in the laboratory without the use of acids. But, in practice, such a method of obtaining hydrogen sulphide has proved inconvenient, as the aluminium hydroxide produced hinders the water, after a time, from gaining access to the remaining sulphide.

The **nitride** is formed when aluminium is strongly heated in a current of nitrogen. It is usually a grey, amorphous compound, which is decomposed by water, ammonia being liberated. However, if the crude nitride is heated in a tungsten tube vacuum furnace at a very high temperature (e.g. 1,890° C.) and at a low pressure—conditions which favour the sublimation of the nitride—it is obtained in the colder parts of the furnace as "rosettes" of colourless hexagonal crystals.[1] The technical method of preparation of the nitride by the action of nitrogen on a mixture of carbon and "bauxite" is referred to in the technical section.

Carbide. At very high temperatures, aluminium combines with carbon, yielding a carbide to which the formula Al_4C_3 has been assigned. It is best prepared by heating aluminium powder with wood charcoal in a crucible. The presence of air is said to play an important part in the reaction.[2] The charcoal mixture is highly porous, and naturally includes much oxygen at the commencement of the process. Apparently some oxidation of the carbon and aluminium is needed to produce the intensely high temperature at which the combination of aluminium and carbon can come about, for the less porous varieties of carbon seem to be less effective. The product contains, besides aluminium carbide, both oxide and nitride. Aluminium carbide reacts with water, producing methane (CH_4), and a little hydrogen,

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

Aluminates. Aluminium hydroxide dissolves readily in a solution of sodium or potassium hydroxide; the solution produced contains an aluminate, such as $NaOH.Al(OH)_3$ or $Na[Al(OH)_4]$, in which alumina seems to function as an acidic oxide. It is, however, a very feeble acid, and the aluminates are much hydrolysed, the solutions being always strongly alkaline towards indicators. Some chemists have regarded them as colloidal solutions of aluminium hydroxide, the alkali being supposed to act merely as a peptizing agent; but careful ultra-microscopic study of the solution has shown that if indeed colloid particles exist in the solution they are too small for detection with the ultra-microscope.[1] The fact that when metallic aluminium is gradually added to a solution of sodium hydroxide, the conductivity of the solution gradually diminishes until the atomic ratio Al : Na becomes equal to unity, after which the conductivity ceases to decline further, has been regarded as evidence that a definite aluminate of the composition $Na[Al(OH)_4]$ is produced.[2] This compound has never been isolated in the solid state, but from solutions very rich in alkali two separate crystalline aluminates have been isolated, which appear to be definite compounds. The following formulæ have been assigned to these bodies by their discoverer[3]:—

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[1] F. Fichter and G. Oesterheld, *Zeitsch. Elektrochem.* **21** (1915), 50.

[2] F. E. Weston and H. R. Ellis, *Trans. Faraday Soc.* **4** (1908), 60.

$4Na_3O.3Al_2O_3.16H_2O$ (diamond-shaped crystals)
$4Na_2O.Al_2O_3.10H_2O$ (needle-shaped crystals)

Most of the "aluminates" described by early investigators were clearly not chemical individuals at all, but mixtures.

The aluminates of the heavy metals are insoluble. They occur in nature as the *spinel* group of minerals, although they are not very easy to prepare artificially; the most important is magnesium aluminate,

Spinel . . $MgO.Al_2O_3$ or $MgAl_2O_4$.

Analytical

Aluminium compounds impart no colour to the Bunsen flame, nor is any single striking reaction known which serves to characterize aluminium salts in aqueous solution.

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[1] R. E. Slade and W. G. Polack, *Trans. Faraday Soc.* 10 (1914), 150.

[2] T. Heyrovský, *Trans. Chem. Soc.* 117 (1920), 1013. Actually it is by no means easy to obtain solutions containing more aluminium than corresponds to the compound $Na[Al(OH)_4]$. The alkaline solution ceases to act upon ordinary aluminium as soon as the atomic ratio Al:Na reaches unity. By the use of amalgamated aluminium, more aluminium hydroxide is brought (for the moment at least) into solution; but the liquid produced is unstable and tends to deposit crystalline aluminium hydroxide, the conductivity increasing as the hydroxide is deposited. At 0° C., the liquid is more stable, and the conductivity may be measured at that temperature. Compare also the work of E. Grobet, *J. Chim. Phys.* **19** (1922), 331.

[3] F. Goudriaan, *Proc. Amst. Acad.* **23** (1920), 129.

Nevertheless the detection of aluminium in solution, and its separation from other metals, does not present any great difficulty. Aluminium is not precipitated by hydrogen sulphide in an acidified solution, but is precipitated as hydroxide by ammonia in the presence of ammonium chloride. These facts serve to separate aluminium from most metals, except iron, chromium, the rare earths, uranium, beryllium, and a few other metals, the hydroxides of which are precipitated under the same circumstances. The separation of aluminium from most of the metals mentioned depends on the fact that they have hydroxides which are undissolved by *hot* caustic soda, a reagent which dissolves aluminium hydroxide yielding an aluminate. Beryllium hydroxide also dissolves in caustic alkali, but is reprecipitated on dilution and prolonged boiling (see page 96). From the clear aluminate solution, aluminium hydroxide may afterwards be precipitated by acidifying with hydrochloric acid and once more boiling with ammonia.

The separation of aluminium from chromium by means of sodium hydroxide is apt to be incomplete and unsatisfactory. For chromium hydroxide also has acidic properties, although the solubility in caustic soda at 100° C. is very small. Consequently many authorities recommend that the chromium should be oxidized to the state of chromic acid, after which aluminium can be precipitated as hydroxide by the addition of ammonia, whilst chromium remains dissolved as ammonium chromate.

Although the methods of separation given above represent the standard procedure, circumstances are known in which they become very incomplete. For instance, if zinc is present in the solution from which aluminium hydroxide is precipitated by means of ammonia, an appreciable amount of zinc may be brought down along with the alumina; in such a case, it may be better to precipitate the aluminium, not by ammonia, but by barium carbonate. The solution is placed in a flask, and sodium carbonate is added until a turbidity appears; a few drops of hydrochloric acid are then added to remove the turbidity. The solution is diluted, barium carbonate is added, and the mixture is shaken and allowed to stand. The barium carbonate keeps the hydrion concentration so low that aluminium is completely precipitated as hydroxide, or as a basic salt, but zinc remains in solution.

When free from other metals, aluminium is almost always precipitated by means of ammonia as the hydroxide, which is afterwards ignited and weighed as oxide (Al_2O_3); care must be taken that no precipitate is lost through spurting whilst the water is being driven off. The ignition can be conducted in contact with the filter-paper.

Before leaving the subject, some remarks must be made upon the precipitation of gelatinous hydroxides. Upon the addition of ammonia to a cold aluminium salt, no precipitate is usually seen at first, since a colloidal solution of the hydroxide is obtained, which requires to be boiled before flocculation occurs. Even boiling may not cause complete precipitation unless ammonium salts are present. If the liquid is filtered before precipitation is complete, hydroxide may pass through the paper and be lost. Moreover gelatinous precipitate may be deposited in the pores of the filter-paper, and may so choke them that filtration becomes a very slow operation. Even under the best conditions the gelatinous hydroxide "filters slowly," and is very difficult to wash free from soluble salts. But this washing must be complete even when no other metal is present in the liquid from which precipitation takes place. For, if the precipitate contains ammonium chloride when it is ignited and burnt, there is a great danger of loss of aluminium as the volatile chloride, $AlCl_3$.

Although the presence of a certain amount of ammonium salts is necessary for the satisfactory precipitation of aluminium hydroxide, the precipitation from solutions containing unduly large quantities of ammonium salts presents considerable difficulty.[1] Under these circumstances a form of hydroxide is produced on boiling, which, although practically insoluble in the filtrate (which contains ammonium salts), is capable of peptization by hot water. If such a precipitate is washed with ordinary distilled water, the result will be inaccurate, and the washing will generally be slow owing to the redeposition of hydroxide in the pores of the filter-paper. It is best to wash the hydroxide produced in the presence of large quantities of ammonium salts, with a 1 per cent. solution of ammonium nitrate. This solution has no solvent action on the precipitate, and when the hydroxide is ignited, the ammonium nitrate is driven off completely, no loss of aluminium resulting.

Aluminium hydroxide can be brought down in a form which settles readily, can be washed by decantation, and presents no trouble in filtration, if sodium thiosulphate is used as the precipitant. For details the original paper should be consulted.[2]

TERRESTRIAL OCCURRENCE

Aluminium is one of the commoner elements occurring in the earth. Complex silicates containing aluminium have crystallized out in all parts of the igneous magma. Of these the felspars and micas, which have already been mentioned in connection with the alkali metals, are, perhaps, the most important.

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[1] S. L. Penfield and D. N. Harper, quoted by Sir W. Crookes, "Select Methods in Chemical Analysis" (Longmans).

[2] J. E. Clennell, *J. Inst. Met.* **28** (1922).

Where igneous rocks containing complex silicate minerals are exposed to the influence of weathering agents, the minerals undergo alteration. The more basic metals (sodium, potassium and calcium) are generally dissolved out and pass into the rivers. This action causes considerable softening of the whole rock-mass, which tends to break up. But the aluminium is not so readily brought into solution, and tends to remain undissolved as particles of various hydrated aluminium silicates ("*clay particles*"). Normally these will be carried off in suspension in the running water, but sometimes they are left behind as beds of "**residual clay**" at the position of the original igneous rock.

Most of the residual clays which are of industrial importance appear to have been formed by the action upon an igneous rock, not of meteoric waters, but of thermal waters and vapours of igneous origin. This has evidently been the case in Cornwall where old granitic rocks, very rich in felspar, have become converted into the famous deposits of

Kaolin (China-clay) . . $Al_2O_3.2SiO_2.2H_2O$.

Uncertainty still prevails as to whether kaolin is a definite compound, although it has become customary to treat it as such.

It is noteworthy that the conversion of felspar to kaolin very often occurs in tin-bearing districts; the ores of tin are also formed by the interaction of vapours with a granitic rock.[1]

In many cases—and especially in tropical climates like India—the decay of igneous rocks under the influence of weathering agencies goes one step farther, and silica is partially removed, leaving residual deposits rich in aluminium hydroxide. Most of the red earthy rocks known as "**laterites**" were formed in this way (but some of the deposits so called are no longer on the site of the igneous rocks from which they were formed, having been moved to their present position by the agency of running water). The red colour of laterite is due to iron hydroxide, derived from the same igneous rocks. Where nearly all the silica has been removed, we get **bauxite**, which is believed to contain the two hydrated oxides.

Gibbsite . . . . . $Al(OH)_3$
and Diaspore . . . . . $AlO(OH)$,

together with a great deal of iron hydroxide, and a certain amount of residual silica. In the "red bauxites," iron is the chief impurity, and is, of course, the cause of the colour. "White bauxites" contain a large amount of silica.

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[1] Compare W. Lindgren, *Trans. Amer. Inst. Min. Eng.* 30 (1900), 614.

Bauxite, which is, technically speaking, the most important ore of aluminium, is found in the tertiary volcanic rocks of the north of Ireland, where it is clearly derived from the acid lava, rhyolite. It occurs in large quantities in the south of France, whilst very important deposits are found in Arkansas, U.S.A., where it seems to be due to the decay of syenites. It is probable that the French deposits—and possibly some of the American ores—are not the direct product of the weathering of igneous rocks. The French bauxites are found in limestones, and it is thought that thermal waters ascending from igneous masses below have carried off aluminium compounds in solution, and have afterwards reacted with the limestones, producing aluminium hydroxide. Important deposits of bauxite also occur in British Guiana, Yugo-Slavia and Rumania.

A rather exceptional product of the decay of felspathic rock is

Alunite, or Alumstone. $K_2SO_4.3Al_2(OH)_4SO_4$,

which has already been mentioned in the section on potassium. It is found in certain regions in Italy, Hungary and the United States, being apparently produced through the weathering of silicate minerals containing aluminium and potassium, by waters containing sulphurous or sulphuric acid; the acids may be derived from the oxidation of minerals like pyrites, or may conceivably be of volcanic origin.

In spite of the commercial importance of the "residual" deposits of aluminium compounds, they are formed only under rather exceptional conditions. The greater part of the aluminium silicate produced when the sodium, potassium and calcium are leached out of igneous rocks by water, is carried off, as fine clay particles, in mechanical suspension (some authorities would say, in colloidal solution). The clay particles pass into the rivers and so out into the sea, where they are dropped on to the bottom, forming fine mud, some little way out from the coast. A good many salts (notably potassium salts) are adsorbed from the sea-water by the clay before it settles; in fact, this adsorption is probably the immediate cause of the settling. In such a way, "**secondary clays**" are formed. Later, during the process of consolidation of the clay-mud into mudstone or shale, the silicates lose water and various mineralogical changes usually take place in the mass. Kaolin tends to disappear, and mica (in microscopic particles) takes its place. Sometimes, owing to great pressure caused by earth-movements, the rock comes to be converted to a **slate**; the pressure causes the mineral particles to arrange themselves with their longer axes in the direction perpendicular to the direction of the pressure, and the rock assumes a "slaty cleavage" recalling the cleavage of crystals, although due to a rather different cause. Finally, when the mineralogical changes caused by heat and pressure become so marked that flakes of mica can be recognized by the naked eye, the rock is called a **mica schist.**

Clays of sedimentary origin—even when comparatively recent and therefore still soft—are naturally more variable in composition (containing many other substances besides kaolinite) than the clays of residual origin.

A few more important aluminium minerals must be mentioned. In certain igneous rocks, and especially near the edge of the intrusive masses, we find the oxide

Corundum . . . . Al_2O_3

and the magnesium aluminate

Spinel . . . . . $MgO.Al_2O_3$.

The crystallization of the free oxide, Al_2O_3, is only to be expected where the igneous magma is unusually weak in silica. It is not surprising to find that corundum occurs especially where igneous rocks are in contact with limestone, the magma having, no doubt, become relatively weak in silica through interaction with the lime. For instance, in the Haliburton district of Ontario, there is evidence of such interaction; for the granitic rocks become abnormally low in silica where they come in contact with limestone, often passing gradually into nepheline-syenites. It is significant that the rocks of the same district contain an important quantity of corundum.[1]

The choicer specimens of corundum and spinel are valued as gemstones; red varieties of corundum are known as "ruby," and blue varieties as "sapphire." A common smoky-black impure variety, which usually contains magnetite, is known as "emery" and forms a valuable abrasive. Many beds of emery are not of igneous origin, having clearly been derived from bauxite by dehydration.

An important mineral occurring in Greenland is the double fluoride,

Cryolite Na_3AlF_6.

It is a transparent mineral resembling ice (hence the name: κρυος = frost, λιθος = stone). It occurs in a large bed in a granitic vein penetrating gneiss.

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[1] F. D. Adams and A. E. Barlow, *Canadian Geol. Surv.*, Mem. 6 (1910), 227.

METALLURGY, TECHNOLOGY AND USES

Manufacture of Metallic Aluminium[1]

Practically the whole of the aluminium metal now manufactured is derived from **bauxite**, although recent attempts to use felspar in Norway[2] and clay in Germany[3] are of great interest. Since bauxite contains, besides oxide of aluminium (alumina), oxides of iron and usually silica, besides minor impurities, the metallurgical process can be divided into two stages :

I. The preparation of pure alumina from bauxite.

II. The electrolytic production of metallic aluminium.

I. **The Preparation of Pure Alumina.** The need for absolutely pure alumina is made imperative by the fact that aluminium in the metallic state cannot be refined ; hence the materials used for its preparation must be free from reducible impurities. The removal of iron is especially important because aluminium containing much iron is apt to be brittle. Two methods are used for obtaining pure alumina :—

(*a*) **Bayer's Process,** suitable for the so-called " red bauxite," in which iron is the chief impurity.

(*b*) **Serpek's Process,** suitable for " white bauxite," which contains a great deal of silica.

(*a*) **Bayer's Process** depends on the solubility of aluminium oxide in caustic alkali. The ore is finely ground, calcined and again ground ; it is then treated with strong caustic soda (specific gravity 1·45) in an autoclave at 150° C. for some hours. The aluminium oxide is dissolved, forming sodium aluminate, whilst the iron, under these conditions, remains as insoluble oxide. The solution is run out of the autoclave, and diluted considerably, the iron oxide and other insoluble matter being filtered off. The diluted solution is now agitated in an autoclave, and slowly suffers hydrolysis, alumina being precipitated ; a small quantity of the precipitate from a previous run is actually added in order to provide nuclei for the process, but nevertheless the hydrolysis requires thirty-six hours. At the end of that period, 70 per cent. of the alumina has been precipitated, and is removed by means of a filter-press, dried, and calcined, yielding anhydrous aluminium oxide.

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[1] See J. T. Pattison, " Aluminium " (Spon, 1918) ; J. Escard, " L'Aluminium dans l'Industrie " (Dunod & Pinat) ; G. Mortimer, " Aluminium " (Pitman, 1919).

[2] See *J. Inst. Met.* 21 (1919), 455.

[3] *Board of Trade J.*, Jan. 17, 1918

The caustic soda solution, still containing some aluminate, is evaporated under reduced pressure until the specific gravity is once more 1·45, when it can be used for extracting fresh bauxite. This process is not very suitable for bauxite containing much silica, because much aluminium is liable to be precipitated in the soda solution as an insoluble sodium aluminium silicate, and will then be filtered off along with the iron.

(*b*) **Serpek's Process** is considered especially suitable for highly siliceous bauxite, although considerable difficulties have been met with in putting it into operation; the method has one great advantage, namely that it produces not only alumina, but also ammonia. Serpek's process depends on the fact that bauxite, heated with carbon at about 1,800° C. in a current of nitrogen, gives aluminium nitride,

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$

The silicon is also reduced to the elementary state, and being volatile at the temperature in question, passes away.

The process is conveniently carried out in slowly revolving cylindrical kilns, similar to those used in the cement industry; but owing to the high temperature needed for the formation of the nitride, the heating is accomplished electrically. The nitride can afterwards be decomposed by water with the production of ammonia and alumina,

$$AlN + 3H_2O = Al(OH)_3 + NH_3,$$

but actually it is quicker to dissolve it in caustic soda, and to recover the alumina by hydrolysis of the sodium aluminate formed, as in Bayer's process.

It is noteworthy that Serpek's process works better with impure bauxite than with a pure mineral. One of the impurities, probably iron, serves as a catalyst for the reaction.

II. **The Electrolytic Production of Aluminium.** When pure alumina has been obtained, the next step is to reduce it to the metallic state. This is invariably accomplished by the electrolysis of a solution of alumina in fused cryolite, Na_3AlF_6 (a mineral which itself contains aluminium). The furnace (Fig. 16) in which the electrolysis is carried out consists of an iron tank, usually lined with refractory material having a low conductivity for heat, and having an inner lining of carbon. The bed of carbon, C, at the bottom, serves as the cathode, whilst the carbon blocks, A, which are suspended from above, and are capable of being raised or lowered, constitute the anodes.

Cryolite, when pure, melts at 1,000°C., but the melting-point is somewhat reduced by the presence of alumina. The electric current has to perform a double function. Firstly, it maintains the temperature high enough to keep the bath fused, and secondly, it causes the electrolytic decomposition of the alumina. The immediate products of decomposition are molten aluminium at the cathode, and oxygen at the anode. Aluminium is a little heavier than the fused bath, and therefore collects at the bottom. In some places the furnaces are periodically tapped, the molten aluminium being run off through the hole T in the base into moulds ; at other works, it is customary to remove the molten metal by means of ladles introduced into the bath from above, one of the anodes being usually raised out of the way during the ladling process.

The oxygen produced at the anode attacks the carbon of the electrodes yielding carbon monoxide and carbon dioxide. The proportion of the gases depends on the temperature. There is more carbon monoxide (and less carbon dioxide and oxygen) in the gases coming off at 1,055° C. than at 945° C. ; it follows that the electrode consumption will be less at the lower temperature.[1] Whatever the temperature, however, the electrodes will certainly be consumed very rapidly, and a factory for producing electrodes is therefore usually established close to each aluminium works. Seeing that aluminium—as stated above—cannot be refined, it is essential to avoid introduction of impurities in the electrodes. They are usually made of a special petroleum coke having a low ash-content.[2]

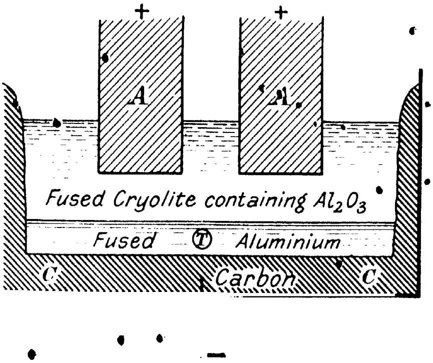

FIG. 16.—Electrolytic Production of Aluminium.

As electrolysis proceeds, the dissolved alumina becomes partly used up, and fresh alumina must be added from time to time. Should the bath become exhausted in oxide, fluorine will be evolved instead of oxygen; even in normal working, a little fluorine is lost, and aluminium fluoride is added occasionally to make up for the loss.

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[1] R. Seligman, *J. Inst. Met.* 17 (1917), 141.

[2] W. Rosenhain, *J. Roy. Soc. Arts,* 68 (1920), 793.

It is a common practice to keep the surface of the bath covered with powdered coke, so as to reduce the loss of heat by radiation.

As a rule, at an aluminium works, 30–50 furnaces will be joined in series, and about 6 to 7 volts is allowed for each furnace, so that the E.M.F. applied to the series is of the order of 200–350 volts. The current required will vary with the size of the furnace, but is usually large. One American installation was designed to send 20,000 amperes through each cell,[1] whilst a German plant near Cologne started during the war was designed for 14,500 amperes.[2] The current efficiency is usually fairly high, considering what a reactive metal is being prepared. At one American works 90–95 per cent. is said to be obtained, but, at some European works, the yield corresponds to a current efficiency of under 70 per cent. Since, however, the P.D. applied to each cell is nearly 7 volts, instead of the theoretical 2·8 volts, the energy efficiency is much lower, commonly 25–40 per cent.

In view of the large amount of electric energy needed for the smelting of aluminium, the industry is mainly restricted to districts furnished with water-power. The alumina prepared from the Irish bauxite, for instance, is electrolysed at a works near the Falls of Foyer in Scotland. The centre of the world's aluminium industry was formerly France, on account of the rich bauxite deposits of that country; but at present the American works (mostly situated at Niagara) supply the greater part of the world's requirements.[3] Several German works were started during the war, which were dependent on coal or lignite for power, but it is doubtful whether manufacture based upon power produced in that way can prove remunerative under normal conditions.[4] Much aluminium is in normal times produced in Switzerland.

Uses of Aluminium and the Light Alloys. The properties of aluminium which determine its practical employment are:—

(1) Its lightness;

(2) its chemical reactivity and affinity for oxygen at *high* temperatures; and

(3) its power to withstand corrosion and retain its lustre in air at *low* temperatures.

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[1] J. W. Richards, *Min. Ind.* **23** (1914), 18.

[2] A. J. Allmand and E. R. Williams, *J. Soc. Chem. Ind.* **38** (1919), 393R.

[3] J. W. Richards, *Met. Chem. Eng.* **17** (1917), 269.

[4] *J. Soc. Chem. Ind.* **39** (1920), 135R; **40** (1921), 380R.

With regard to the first property, it is the lightest of all the metals in daily use, and this would at once suggest its use in aeroplane-building, and for other purposes where weight must be reduced to a minimum. But, for all constructional work, the total weight of metal needed is determined not merely by the specific gravity but also by the strength, since clearly, if the material is a weak one, stouter pieces will have to be employed. Now, although pure aluminium is by no means the weakest of metals, its strength can be increased greatly by alloying certain other metals with it, and consequently aluminium alloys are generally used in the place of pure aluminium where a minimum weight is required.

Some of the light alloys advocated before and during the war were not found to fulfil the claims of their supporters. As a matter of fact, many metals, when added to aluminium, although strengthening it considerably, reduce the ductility unduly. An important exception is zinc, which when added in any proportion up to about 18 per cent. forms an alloy consisting (if slowly cooled or annealed so as to obtain equilibrium conditions) of a single homogeneous solid solution.[1] It has been stated that an alloy with 13 per cent. zinc has a ductility (as measured by the elongation) nearly as great as that of pure aluminium, whilst it has about twice the strength of the pure metal.[2] Small amounts of copper are also added with advantage to the alloys of zinc and aluminium; it increases the tenacity and rigidity.

The earlier German Zeppelins were built of a light alloy with a strength only slightly inferior to that of mild steel; later, alloys were used, in this country, for the construction of aeroplanes with a very much greater strength. The following alloys have been recommended by the workers at the National Physical Laboratory[3]:—

For castings, Al $82\frac{1}{2}$–$85\frac{1}{2}$%, Zn 12–15%, Cu $2\frac{1}{2}$%
For rolling, Al 77%, Zn 20%, Cu 3%

The addition of small quantities of magnesium (0·5 per cent.) to some of these alloys has been found advantageous.

Many of the aluminium alloys containing zinc—although possessing very valuable mechanical properties—are somewhat liable to corrosion; moreover they lose their strength at high temperatures. Much work has been carried out in the investigation of classes of light alloys which are not open to these objections. Alloys of aluminium with copper, or with copper and nickel, have given results in some respects promising. Copper produces a greater effect on aluminium than does zinc, 6 per cent. of copper having a hardening action equal to that of 13 per cent. of zinc; but copper produces a considerable decrease in the ductility.[1] One of the best-known light alloys is called "duralumin"; it contains 4 per cent. copper, 0·5 per cent. magnesium and 0·5 per cent. manganese.

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[1] For equilibrium diagram see D. Hanson and M. L. V. Gayler, *J. Inst. Met.* (1922). Compare W. Rosenhain and S. L. Archbutt, *Phil. Trans.* **211** [A] (1911), 315; O. Bauer and O. Vogel, *Mitt. Kgl. Mat. Prüfungsamt*, **33** (1915), 146.

[2] H. Schirmeister, *Stahl u. Eisen*, **25** (1915), 650.

[3] W. Rosenhain, *J. Roy. Soc. Arts*, **68** (1920), 805, 819.

A large class of light alloys are those containing magnesium as an important constituent. The addition of magnesium (up to 19 per cent.) to aluminium increases the hardness and tensile strength without seriously affecting the ductility.[2] One of the earliest of the light materials to be introduced ("magnalium") consisted essentially of magnesium and aluminium. Simple binary alloys of this character are no longer in favour, but alloys containing aluminium and magnesium along with other elements, such as silicon, copper or nickel, have their supporters. A material known as "Y-alloy," containing 4 per cent. copper, 2 per cent. nickel and 1½ per cent. magnesium, has received special commendation.[3]

Certain alloys of aluminium, notably those containing magnesium and silicon, have the property of "**age-hardening**"; when quenched these alloys are soft, but become hard after being stored for a few days.[4] The cause of age-hardening appears to be connected with the separation of very small particles of some hard constituent within the grains of solid solution of which the material is composed. It may happen that the rapid cooling may render the solid solution supersaturated with regard to one constituent. During the quenching, there is no time for the constituent to be thrown out as a separate phase, but when the alloy is stored at ordinary temperature, this constituent is precipitated as a very large number of minute particles, probably of colloidal size. If the constituent precipitated is itself fairly hard, the presence of these particles greatly interferes with the deformation of the material; for the presence of a hard particle on any plane along which slip might occur in a homogeneous crystal, necessarily prevents the two halves of the crystal from gliding over one another. Now if the particles produced are very small and therefore very numerous, nearly all planes of possible gliding will be obstructed in this way;

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[1] M. Waehlert, *Met. u. Erz.* **18** (1921), 298.

[2] See curves given by Hanszel, *Zeitsch. Metallkunde* **13** (1921), 319.

[3] W. Rosenhain, S. L. Archbutt and D. Hanson, *Engineering*, **112** (1921), 613, 644.

[4] D. Hanson and M. L. V. Gayler, *J. Inst. Met.* **26** (1921), 321; **27** (1922), 267; Z. Jeffries and R. S. Archer, *Met. Chem. Eng.* **24** (1921), 1057; **26** (1922), 249.

and consequently the hardness and strength of the material will increase with age. It is noteworthy that if the very small particles afterwards coalesce to form a smaller number of large particles, the interference with gliding will decrease, since a smaller number of possible gliding-planes will be obstructed; this occurs in certain alloys of aluminium and zinc, in which the hardness increases quickly after quenching, and then falls again.

The composition of the small hard particles which appear during "age-hardening" varies in different cases. The hardening of alloys with magnesium and silicon is due to the appearance of the compound Mg_2Si, whilst that of duralumin seems to be connected with $CuAl_2$. Both compounds are much more soluble at 500° C. than at lower temperatures, and thus the precipitation of the substances in the quenched alloys on storage is not surprising.

The light aluminium alloys are used to a very considerable extent in automobile construction. In America the standard alloy for motor castings is said to be a binary alloy composed of

Al 92%, Cu 8%,

whilst in this country an alloy containing zinc as well as copper,

Al 87–90%, Zn 8–10%, Cu 2–3%

is preferred.[1] In general, wherever there is frequent stopping and starting of any object, a saving of energy will be effected by making that object as light as possible.[2] It needs, for instance, less energy to start an electric train with the metallic parts made of an aluminium alloy than a similar train in which steel is employed. For a similar reason, the employment of aluminium alloys in the construction of bicycles and other road vehicles, agricultural machines, artificial limbs, the moving parts of sewing-machines and similar objects, is perfectly rational. In the case of fixed objects, however, the use of aluminium is less justifiable. A bridge constructed of aluminium alloy could—it is true—have spans about three times as long as a similar bridge of steel, owing to the lightness of the former material; but, in spite of that fact, the steel bridge will almost certainly be cheaper, and probably more reliable; there is no advantage in using aluminium for such purposes.

Another use of aluminium is to replace copper for electrical purposes, especially for transmission lines and for telegraph and telephone wires.[3] Here pure aluminium is generally employed. The specific conductivity of aluminium is less than that of copper, and consequently a stouter conductor is required; nevertheless, on account of the low specific gravity of the aluminium, the weight of aluminium demanded for a line of given conductivity is only half the weight of copper. Consequently the cost of the material for a line constructed of aluminium will be less than a line of copper of equal resistance, whenever the price of aluminium is less than double the price of copper. On the other hand, aluminium has certain practical disadvantages. The making of joints is far more difficult with aluminium than with copper. Furthermore, there is —in aluminium—a distinct danger of corrosion, especially at the joints, where corrosion couples may be set up.

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[1] E. C. Hill, *Mech. World*, **68** (1920), 169.

[2] W. Rosenhain, *J. Soc. Chem. Ind.* **37** (1918), 340R.

[3] E. V. Pannell, *J. Amer. Inst. Met.* **9** (1915), 167; Wunder, *Zeitsch. Metallkunde*, **13** (1921), 179.

There is a considerable future for aluminium in the electrical industry, in spite of the comparative difficulty in making good contacts between aluminium conductors. Aluminium wire has been used extensively for winding coils. On account of its lightness it is specially suitable for winding the moving coils of dynamos and motors.[1] For the fixed coils, there is less advantage in using the light metal.

The applications of aluminium depending on its chemical properties need only shortly be referred to. Chiefly in the form of dust, it is often used instead of zinc, in metallurgy, for precipitating gold and silver from cyanide solutions. It is also used very largely as a deoxidizer for steel and other metals, being added to the metal previous to casting, in order to combine with the oxygen which would otherwise cause intergranular weakness.

Advantage of the affinity of aluminium for oxygen is also taken in the *thermite welding* of steel, especially useful for tramway-rails; a mixture of aluminium powder and iron oxide contained in a funnel-shaped crucible lined with magnesia, is allowed to react according to the equation,

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe.$$

The reaction is started by means of a stick of magnesium which is pushed into mixture and lit by a match. The great heat generated by the reaction serves to raise the temperature far above the melting-point of iron, and the metallic iron produced by the reaction is in a very fluid state. When the whole material is molten, a plug at the bottom of the crucible is withdrawn, and the molten iron is allowed to flow round the junction of the rails or bars to be welded together, the junction having previously been surrounded by a mould of refractory earth, which serves to retain the molten iron in position and to retard the cooling; when the whole has solidified, a strong join is obtained.

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[1] Compare P. Askenasy, *Zeitsch. Elektrochem.* **22** (1916), 294.

A similar reaction is sometimes used for the preparation of such metals as chromium and manganese from their oxides.

The intense heat of oxidation of aluminium has been used in explosive mixtures. *Ammonal*, for instance, contains aluminium powder, ammonium nitrate and a high explosive such as trinitrotoluol. When the mixture explodes, the aluminium is oxidized by the ammonium nitrate, and the temperature becomes very high. Ammonal is essentially a heat-producing explosive.

Seeing that there are so many uses of aluminium which depend on its affinity for oxygen, the applications which are based upon the alleged non-corroding nature of the metal require to be carefully considered. As already stated, the non-corroding character of aluminium is connected with the oxide film upon the surface, and is therefore less to be relied on than if it were a specific property of the metal itself. The metal may prove perfectly immune to corrosion for a time, and then suddenly fail owing to some apparently trifling alteration of the conditions. For instance, aluminium has been largely used in German breweries as a material for various large vessels employed in brewing, and has normally proved entirely satisfactory. But, at one brewery, a small thermometer happened to get broken, and a few drops of mercury came in contact with the metal. Failure quickly followed.

Aluminium vessels are used with success in industrial organic chemistry, especially in the manufacture of glue, gelatine, and various organic acids. One advantage over other metals is that even if slight corrosion does occur, the salts of aluminium are both colourless and non-poisonous, and do not spoil the products. For the same reason, the use of aluminium vessels in cookery has proved satisfactory, although aluminium is by no means unattacked by vegetable juices, which have usually an alkaline reaction.

The point to ensure, however, is that the corrosion which does occur shall be of a uniform character and spread over the whole surface. If pitting occurs, an aluminium vessel may quickly be perforated even though the total amount of metal oxidized is small. It is found that cold-worked aluminium—probably owing to variations of the potential at different parts of the surface—is corroded in a particularly objectionable manner, local bulging and blistering of the surface being produced.[1] The bulging is probably due in part to the internal stresses always present in cold-rolled metals, which stresses cease to balance one another when the outer layer of the metal has been removed by corrosion; the deterioration of cold-worked metal due to this cause has already been discussed in Volume I, Chapter II. It is certainly found that cold-worked aluminium articles, if properly annealed so as to remove internal stresses, generally corrode in a uniform and comparatively harmless manner.[1] There may, however, be other causes for the blistering and pitting of aluminium sheet. It occasionally occurs even in thoroughly annealed aluminium, and seems then to be connected with the presence of minute gas-cavities with which aluminium sheet is usually permeated. If water or solution gains access to these cavities, the formation of aluminium hydroxide may occur, and, as this is more voluminous than metallic aluminium, local expansion and blistering must occur.[2] Moreover, the presence of the corrosion product—in any form other than that of a waterproof coating extending over the whole surface—appears actually to be favourable to corrosion, for the reasons suggested in Chapter XIV (Vol. I). Therefore, when once corrosion has fairly started on the site of one of these gas-cavities, it continues to bore down into the metal until the sheet becomes perforated.

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[1] E. Heyn, *J. Inst. Met.* **12** (1914), 26.

It should be mentioned that the corrosion of aluminium can largely be avoided by treatment with a suitable paint or varnish.

There are several other problems to be overcome in connection with the general employment of aluminium, mostly caused by the existence of the oxide-film. It is somewhat difficult to solder aluminium, as no flux is known which will dissolve away the oxide in an entirely satisfactory manner, and thus allow good mechanical continuity at the joint. In practice, it is necessary to remove the oxide-skin by abrasion.[3] Even when the soldering has been satisfactorily performed, and the article is put to use, the contact of the solder with the aluminium is liable to set up a "corrosion couple." The welding of aluminium has also presented difficulty, on account of the presence of the oxide-film, although devices are known by which this difficulty can, in many cases, be overcome.[4]

Similarly, it is very difficult to deposit an adherent coating of another metal—nickel for instance—upon aluminium by electrolysis, although a good method of nickel-plating upon aluminium would overcome many of the corrosion troubles which have been described above. Methods by which the surface is treated with hydrochloric acid, potassium cyanide, or other corrosive substance just before nickel-plating, have been described, but are not considered entirely satisfactory; more recently ferric chloride has been advocated for the preparation of the aluminium. It is probable that the main function of the corrosive substance is to produce pitting on the aluminium surface, and that the nickel deposit thus "interlocks" with the aluminium. This being the case, it is natural to consider whether the pitting could not be produced more conveniently by mechanical means. Recently a process [1] has been worked out in which the aluminium is first roughened by means of a high-pressure sand-blast, a rather fine variety of sand being used. Afterwards it is nickel-plated in an ordinary plating bath, and good adhesion is said to be obtained.

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[1] E. Heyn and O. Bauer, *Mitt. Kgl. Mat. Prüfungsamt*, **29** (1911), 2.

[2] R. Seligman and P. Williams, *J. Inst. Met.* **23** (1920), 159, especially p. 168. The further views developed by these writers who think that the cavities act mainly through retaining hydrogen peroxide—which is at once the product of corrosion and the promoter of it—are not altogether free from possible objections; however, the paper deserves careful study.

[3] E. Andrews, *Amer. Machinist*, **54** (1921), 167E.

[4] C. E. Skinner and L. W. Chubb, *Trans. Amer. Electrochem. Soc.* **26** (1914), 149. See also *Chem. Zeit.* **83** (1914), 886. Also J. Escard, "L'Aluminium dans l'Industrie" (Dunod and Pinot), 1918).

It has been stated above that the oxide-film upon aluminium occasionally makes it rather difficult to obtain a thoroughly good electrical contact with that metal. Advantage is sometimes taken of this fact to obtain an insulating layer on aluminium wire. The wire can be covered with a film of considerable resistance by anodic treatment in a solution containing borax or sodium silicate, a high voltage (200–400 volts) being applied to the bath. The character of the film produced upon the aluminium wire has already been discussed in the section on valve-action (Vol. I, page 389). Aluminium wire treated in this way can be used, without further covering, for winding coils in which insulated wire would usually be employed. The film will withstand voltages up to about 200 volts without appreciable electrical leakage at low temperatures.[2] The insulation is apt to break down if the wire becomes unduly hot.

The light alloys in which aluminium is the main constituent have already been discussed. Another important alloy of aluminium, namely aluminium bronze, which contains only about 10 per cent. of aluminium and about 90 per cent. of copper, will be discussed in the section dealing with copper (Vol. IV).

Aluminium Leaf and Powder. Aluminium is to a considerable extent converted to the form of fine leaf, which is largely employed for the wrapping of chocolate. It is also reduced to powder, which finds application both as a pigment and—as already stated—as a chemical reagent. Aluminium bronze powder is also a useful pigment. Various methods are used for preparing the powder.[3] Where it is intended for employment as a pigment, it is best to start with aluminium in the form of leaf or paper, which receives comminution in a special form of stamp mill. This produces microscopic flakes which are very much thinner in one direction than in the others. It is necessary to add wax or stearine to the mixture to prevent the particles from welding together. The aluminium powder then passes through a special polishing machine, where the surfaces of the flakes acquire a high polish. The polishing operation is somewhat dangerous, because the fine dust, when suspended in air, forms an explosive mixture, and several serious explosions have occurred at the mills through the ignition of such mixtures, probably by an electric spark from the machinery. The danger is certainly increased by the presence of moisture in the air, and of carbide in the metal; for moisture acts on pure aluminium producing hydrogen, whilst if carbide is present, it is attacked yet more rapidly, hydrocarbons being evolved.[1]

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[1] L. Guillet and M. Gasnier, *Comptes Rend.* **170** (1920), 1253. For a new chemical method of treatment, see A. Mazuir, *Ann. Chim. Anal.* **2** (1920), 335.

[2] C. E. Skinner and L. W. Chubb, *Trans. Amer. Electrochem. Soc.* **26** (1914), 137.

[3] *Mech. World*, **60** (1916), 29.

Aluminium paint has proved excellent for protecting iron-work from rust. Owing to the high coefficient of expansion of aluminium, the paint does not crack when the iron-work becomes hot, as do paints containing non-metallic pigments.

Manufacture and Uses of Aluminium Compounds

In addition to the use of bauxite as an ore of aluminium, a certain amount is used as a refractory for the lining of furnaces. A larger quantity is used in the manufacture of aluminium salts. Pure aluminium salts can be prepared from the purified alumina, obtained from bauxite by the methods which have already been discussed. Another useful source of the soluble salts is the mineral

Alunite . $K_2SO_4.3(AlO)_2SO_4.6H_2O$,

a basic sulphate which is soluble in sulphuric acid. The solution on crystallization yields **potash alum**, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, which, being less soluble than most of the aluminium salts, can readily be purified by recrystallization. An alternative method of treating alunite now used in America consists in roasting the mineral so as to drive off part of the sulphur trioxide, followed by leaching with water; potassium sulphate passes into solution, whilst alumina remains undissolved.[2]

Aluminium sulphate is largely made by treating china clay with hot strong sulphuric acid. An impure variety of alum was formerly produced from the so-called "alum shales," and this industry still survives to a small extent. Alum shales are bituminous shales containing iron pyrites (FeS_2). By weathering or gentle roasting, the sulphur can be oxidized to trioxide, which decomposes the aluminium silicate, yielding the sulphate. The oxidized product is leached with water, and by adding potassium sulphate or ammonium sulphate to the product, an alum is obtained; the alum produced from this source usually contains iron.

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[1] See *U.S. Bur. Mines*, Technical Paper **152** (1918); R. J. Zink, *Chem. Zeit.* **35** (1911), 1370.

[2] *J. Soc. Chem. Ind.* **40** (1921), 407R.

The main applications of aluminium salts can be attributed to the action of aluminium ions upon colloidal substances. It was pointed out in Chapter VII (Vol. I), that a trace of a salt of aluminium or other trivalent metal, added to a liquid containing negative colloid particles, deprive the particles of their charge, and causes flocculation. This fact has been applied to the purification of drinking-water containing suspended matter. If a little aluminium sulphate is added to the water, the suspended matter, whether consisting of "clayey" particles, or of organic colloids, quickly settles to the bottom; a large proportion of the bacteria in the water are carried down with the rest of the sediment, and the water is thus rendered safer for drinking purposes. In other cases, aluminium salts are added to water of Moorland origin to remove the colour, which is due to particles of colloidal size. Under the influence of the aluminium ions, the colloid particles collect into flocks which can be removed by settling or by filtration.[1] A similar process is very largely employed for the treatment of sewage and industrial effluents. The employment of pure aluminium sulphate, or pure alum, is not essential. A crude mixture of aluminium and iron sulphates, known as "*alumino-ferric cake*," made by the direct solution of bauxite in sulphuric acid, serves the purpose almost as well; ferric iron ions act in the same way as aluminium ions, but are rather less effective.

The hardening action of aluminium salts upon gelatinous matter, such as exists in hides, is, no doubt, closely connected with the flocculating action upon sols. Aluminium sulphate, or alum, is used in the process of *alum tanning*, or *tawing*, employed for the preparation of white kid leathers. It is interesting to note that the salts of other trivalent metals also are used in tanning, notably the salts of chromium and iron.

Similarly, aluminium salts are largely used, along with organic colloids, in the *sizing* of paper. Many papers intended for printing purposes are coated with a preparation of "rosin soap," to which aluminium sulphate has been added to render the rosin hard and insoluble.

Likewise, aluminium salts are used as *mordants* in dyeing, for the "fixing" of certain dyes which would wash out if the fabric were merely steeped in the dye solution. They are only useful for dyes in which the colloid particles have a negative charge. Such dyes form solutions in water, but the solutions are flocculated by the addition of aluminium salts, the charge on the particles being removed by adsorption of aluminium ions. Since dye-stuffs of this class have usually an acid character, the same fact may be expressed in a different way, by saying that an insoluble aluminium salt of the acid in question has been produced. The precipitate produced by adding aluminium salts to an acid dye-stuff invariably contains aluminium, and can correctly be regarded as an aluminium salt of the dye-acid, but not, in general, as an aluminium salt of definite composition. The controversy regarding the theory of mordants is, like most other controversies in colloid chemistry, mainly a question of nomenclature; several analogous cases were discussed in Chapter VII (Vol. I).

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[1] J. Race, *J. Soc. Chem. Ind.* **40** (1921), 150T.

The application of an aluminium salt to the fabric takes place before the dye is applied. In one method, cotton goods are soaked in an aluminium acetate solution, and are then hung up in a warm place so that hydrolysis sets in, aluminium hydroxide or a basic salt being precipitated. The cotton is next soaked in the solution of the dye-stuff, and the latter is precipitated by the aluminium compound within the fibres of the cotton. Thus the dye is rendered insoluble, and will not "wash out" when the dyed material becomes wet.

It is worth while to point out that other polyvalent salts, notably those of tin, iron and chromium, are also employed as mordants.

The precipitates obtained by the interaction of an aluminium salt with a suitable dye-stuff in the presence of alkali are sometimes used as pigments, under the name "lakes"; they are less permanent to light than the true inorganic pigments.

Abrasives. The extreme hardness of strongly heated aluminium oxide makes it useful as an abrasive. The natural deposits of emery have, of course, long been utilized, but are inadequate for the present demand. Artificial abrasives are now prepared by heating bauxite with carbon in the electric furnace at a very high temperature; the oxides of iron and silicon are largely reduced to the elementary state, and are obtained as a technically useful alloy (ferro-silicon), whilst the less easily reducible alumina is merely fused, and solidifies to a mass which is said to be harder than natural corundum.

It may here be mentioned that the manufacture of artificial gem-stones has been carried out on a comparatively large scale. Before the war, a Boulogne works was said to be preparing 1,000 kilograms of rubies yearly, by melting up in an oxy-hydrogen flame alumina, fluorspar, and a trace of chromium oxide, the chromium being responsible for the red colour of the gem-stone.[1]

Ultramarine. Several blue minerals (haüyne, nosean, lasurite, etc.) consisting of complex silicates of aluminium, sodium and other metals, but always containing sulphur, occur in igneous rocks. Where they are found in sufficient quantities as to be commercially important, as in the Kokcha valley (Central Asia), they are known as "lapis lazuli"; such deposits were at one time eagerly sought after, being ground up to form the blue pigment "ultramarine."

Ultramarine is now, however, prepared artifically, and by varying the conditions of manufacture different shades of blue, and also of green and red, can be obtained.

There are two kinds of ultramarine made, distinguished by their silica content. The variety with the lower silicate-content is made by heating a mixture of china clay, sodium sulphate, and charcoal (or tar) in a crucible or muffle furnace. At first a white substance is produced; this turns gradually to a green substance, which becomes blue when a further quantity of sulphur is added to the mixture. To obtain the high-silica variety, sand must be added to the charge, and sodium carbonate is used instead of sulphate. The product is ground very finely before being sent out from the works. Ultramarine is used as a water-colour and oil-colour, as well as in calico-printing and in wallpaper; it is also employed to "whiten" paper, i.e. to hide the yellow colour normally present, and is added, for a similar purpose, to sugar.

A great deal of uncertainty still exists regarding the exact nature of the various ultramarine products. Some of the changes which they undergo are of great interest. Blue ultramarine is turned violet when heated in chlorine gas, and the further action of nitric acid vapour turns it red. Most varieties of ultramarine are decomposed by dilute acids, silica being liberated in the gelatinous state; some sulphuretted hydrogen is as a rule evolved, although much of the sulphur is precipitated in the elementary condition, in a very fine state of division.

By the action of silver salts upon ultramarine, silver replaces the sodium. It is noteworthy also that ultramarine can be produced in which boron takes the place of aluminium.[2] The interchange of elements recalls that occurring among the zeolites (hydrated silicates), and it is generally believed that the ultramarines are related to the zeolites, sodium sulphide taking the place of the water invariably present in the zeolites.[1] Many zeolites yield blue or green bodies when treated with sodium sulphide; "permutit," for instance, gives a greenish body with sodium sulphide. It is very doubtful whether all the different ultramarines which have been described are really definite compounds. The cause of the blue colour has been attributed to colloidal particles of free sulphur suspended in the silicate mass, and this explanation—although not universally accepted—appears very plausible.[2] It at least suggests a reason why so many bodies of highly diverse composition, having very little in common except the presence of free sulphur, should all show this colour; and, at the same time, it explains why comparatively small changes of environment, such as might be expected to affect the size and character of the colloid particles, have a striking effect upon the colour. It is noteworthy, moreover, that colloidal particles of sulphur in a glass may confer a blue colour, just as colloidal selenium confers a red colour.[3]

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[1] B. Neumann, "Chemische Technologie" (Hirzel), 1912 edition, p. 284.

[2] J. Hoffmann, *Chem. Zeit.* 34 (1910), 821.

✓The Ceramic Industry

Ceramic art consists essentially in preparing a plastic mass of clay and water, pressing it into the required shape, drying the article thus prepared, and then burning it at such a high temperature that the clay particles fuse or soften, at least superficially, so as to adhere together; thus the article, after cooling, possesses rigidity and considerable strength. It is convenient to include in the general term "ceramic industry," the making of articles such as magnesite firebricks, where the same principles are involved, but in which the essential material is not clay.

The products of the ceramic industry are many and various, and, before discussing the matter further, some sort of rough classification must be offered. Many attempts have been made to classify ceramic products, and all are, in some respects, unsatisfactory. The following classification, although far from perfect, will suit our purpose:—

I. Materials of High Softening-point (Refractories).

Fireclay Silica Calcined magnesite Calcined dolomite Calcined bauxite Chromite Zirconia	used for	Firebricks Furnace linings Glass-pots Gas-retorts Zinc-retorts Muffles Crucibles etc.

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[1] L. Bock, *Zeitsch. Angew. Chem.* **28** (1915), i. 447; **30** (1917), i. 161; **33** (1920), i. 23.

[2] P. Rohland, *Koll. Zeitsch.* **16** (1915), 145.

[3] W. D. Bancroft, *J. Phys. Chem.* **23** (1919), 616.

II. Mixtures containing Materials of Comparatively Low Softening-point.

A. Porous Body (**Terra-cotta** or **earthenware**), used for:—

Unglazed.	*Glazed.*
Builder's bricks	Glazed bricks
Unglazed tiles	Glazed tiles
Porous water jars (Eastern)	Faience for—
Battery jars	table ware
Filters	flower vases
	decorative purposes

B. Nearly non-porous body, vitrified ground-mass, opaque (**Stoneware**), used for:—

Unglazed.	*Glazed.*
Certain paving tiles	Drain pipes
Vitrified bricks	Sanitary ware
Some fine stoneware	Stoneware bottles for food and drink
	Chemical stoneware
	Some fine stoneware

C. Non-porous body, almost wholly vitrified, translucent (**Porcelain**).

Unglazed.	*Glazed.*
(1) **Soft** "Parian"	English Bone China
	Continental Soft Porcelain (Seger's Porcelain, etc.)
(2) **Hard** "Biscuit"	Continental Hard Porcelain (Meissen, etc.)
	Laboratory dishes and crucibles
	Electric insulators

The distinction between the different classes is not a sharp one; in some kinds of stoneware, the body is almost as porous as in earthenware. The differences in porosity are regulated partly by the choice of composition of the plastic mixture employed, but mainly by the temperature of firing. If the mass is heated so that the particles fuse only superficially, and adhere together at the points of contact, the resulting mass will be porous, and **terra-cotta** or **earthenware** results. If the heating is sufficiently intense to cause some constituents of the mixture to become fused, the liquid filling up the spaces between the larger or more refractory particles, the body will be comparatively impermeable, but, owing to its heterogeneous character, it will be opaque to light; thus we get **stoneware.** If the temperature of firing be still higher, so that a larger proportion of the mass is fused, the resultant body may be translucent (**porcelain**), since the amount of suspended unfused matter is less. In the extreme case, hard porcelain, the greater part of the constituents undergo vitrification at the temperature of firing, so that the character of the mass approaches both in translucency, hardness and composition that of a milky glass, i.e. a devitrified glass. Probably only a small proportion of the original grains of the plastic mixture survive in hard porcelain; the micro-sections, however, show crystals of sillimanite, $Al_2O_3.SiO_2$, which has crystallized out from the mass at some stage of the manufacture.

Qualities required in Raw Materials. The three properties required of a ceramic mixture are :—

(1) **Plasticity**; the property which enables the material when mixed with water to be formed by gentle pressure into any shape required without "cracking" or collapsing.

(2) The property which enables the article to retain that shape even after drying.

(3) The property which enables the article so prepared, to attain strength and absolute rigidity, when "fired" at a high temperature; this depends on the power of the particles to undergo at least superficial fusion at the points where they are in contact.

The peculiar fitness of "clayey" substances for ceramic purposes is due to the fact that they possess these properties in a very marked degree. Many of the substances used for making refractories (e.g. calcined magnesite) are not sufficiently plastic even for moulding into the simplest forms, and, in any case, would not keep their shape when dried; in such cases, it may be necessary to add some carbonaceous "agglomerant," like tar, glue, starch, or dextrin as a binder, the organic body being decomposed and driven off when the articles are burnt. The same materials also require an exceptionally high temperature to produce the superficial fusion of the particles, and sometimes it may be necessary to introduce a fluxing agent into the mixture.

The cause of the special value of clay for ceramic purposes has been a subject of much discussion.[1] The quality of plasticity, as defined above, is shown to some extent by most insoluble powders when mixed with water; the particles stick together when wet, forming a "paste," which can be moulded into almost any required shape; but in ordinary cases, they fall apart when the water evaporates. There is no doubt, therefore, that the adhesion of the particles to one another is not direct, but depends on the water film between the particles. It is easy to make the particles slide over one another—as occurs when the mass is moulded into shape—without destroying the watery film between them. But to tear one particle away from its neighbour would involve the disruption of the watery film; moreover, the tearing will involve an increase in the free surface of the water, and would involve an increase of surface energy. Thus the "pastes" can be moulded into form without cracking.

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[1] Two recent papers, which embrace views slightly different from those advanced in this book, may be mentioned. J. W. Mellor, *Trans. Faraday Soc.* **17** (1922), 354; N. M. Comber, *J. Soc. Chem. Ind.* **41** (1922), 77T. See also F. F. Grout and F. Poppe, *Trans. Amer. Ceram. Soc.* **14** (1912), 71.

However, when we are dealing with particles of very small size, a second type of attraction may occur [1]; this is due to the molecular forces operating directly between the surface molecules or atoms of the particles where they come into contact. We can only expect this direct attraction to be important where the surface of contact is large compared to the mass of the particle; and since the ratio of surface to mass increases as the particles become smaller, we observe the direct type of adhesion best in particles of ultra-microscopic size.[2] The characteristic "stickiness" of "colloid" substances is of this nature; the practical usefulness of a gum solution, for instance, depends on the fact that the adhesive forces between the gum particles persist after the water has evaporated.

Now in clays we are concerned with particles of intermediate size; they are smaller than those of typical powders, and are indeed small enough to show many "colloidal phenomena"—such as cataphoresis and flocculation by electrolytes; nevertheless they are considerably larger on the average than particles of "typical colloids." We may therefore expect both the indirect and the direct types of adhesion to occur, and it is natural to attribute to the first mode of adhesion the plasticity of the clay shown whilst wet, and to the second, the fact that the moulded articles retain strength when dried.

There are, as explained in the section upon the "terrestrial occurrence" of aluminium, two main varieties of clay:—

(1) **Residual clays** ("China clay," etc.), consisting essentially of kaolin particles.

(2) **Secondary clays** ("Ball clays," etc.), in which the most important constituent is believed to be mica in minute crystals.

Now it has long been known to potters that the residual clays, although in many respects more valuable than the others, are generally less plastic, and feel less "unctuous to the touch." This is easily understood on the view of plasticity suggested above, because the kaolin grains of the primary clays are larger; moreover, mica-flakes have an unusually large surface compared to their volume, and their form is such that they adhere together readily when separated by the thin film of water, and yet can glide over one another easily when the mass is pressed into shape. Other substances, such as powdered talc, which consist of particles of flaky or lamellar shape, yield unusually plastic mixtures when moistened with water [1]; but in general the strength vanishes when the water evaporates. If ordinary mica is ground to an impalpable powder and mixed with water, the pulp has a plasticity equal to that of many clays [2]—a fact that supports the view that the plasticity of ordinary clays is connected with the form of the particles. The adherence of the mica-flakes may perhaps be compared to the "sticking together" of fragments of wet paper, although the two cases are not entirely the same. The moderate plasticity of kaolinitic clays has also been ascribed to the plate-like form of the kaolin particles.

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[1] U. R. Evans, *Trans. Faraday Soc.* 18 (1922), 76.

[2] An attraction which is probably of the direct type is observed between objects of quite large size where the surfaces are exceptionally smooth and quite clean. Thus two absolutely flat plates pressed together will "seize" and unite, but if the surfaces are not absolutely flat and smooth, the plates will only come into true contact at a few points and no union will result.

Although this indirect mode of adhesion may serve to explain to a large extent the behaviour of clay whilst wet, yet it can scarcely explain why articles moulded from plastic clay (unlike those moulded from artificially prepared plastic mixtures such as powdered talc and water) retain their rigidity even after drying. Here we seem to be dealing with the "direct" type of adhesional force, such as operates in typical colloids. Many chemists consider that a film of colloidal matter, possibly silicic acid, aluminium hydroxide or ferric hydroxide, exists round the particles, which serves to bind them together after drying, just as colloidal silica is believed by the same chemists to be the actual binding agent in Portland Cement. The theory has not been worked out very fully, and there are still several points unexplained.[3] It is just possible that the colloidal matter may consist of organic substances; certainly the character of some clays is altered considerably when they are treated with solvents which would remove organic matter.[4] On the other hand, it is not impossible that the colloidal particles which function as the "adhesive" may actually be minute clay-particles, having the same composition as the larger ones.

Highly plastic clays are said to be "fat," whilst the less plastic clays are said to be "lean." No clays consist entirely of kaolin or mica particles. Residual clays contain some of the other constituents of the original rocks from which they were derived, quartz and felspar, for instance. These minerals have no plastic qualities, but they can largely be removed, if desired, by washing or by "osmose" (see below). The special value of certain residual china clays—such as those of Cornwall—is that, when the clay particles have been concentrated by washing, they consist mainly of a pure kaolin; the product has, therefore, a high softening-point, and, being almost free from iron, yields a wonderfully white body; such clays are useful for making porcelain. On the other hand, secondary clays can rarely be washed so pure as to give a colourless body.

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[1] H. A. Wheeler, *Miss. Geol. Surv.* **11** (1896), 97; A. Atterberg, *Zeitsch. Angew. Chem.* **24** (1911), 928.

[2] R. T. Stull, *Trans. Amer. Ceram. Soc.* **4** (1902), 255.

[3] N. B. Davis, *Trans. Amer. Ceram. Soc.* **16** (1914), 65. See also W. D. Bancroft, *J. Ind. Eng. Chem.* **12** (1920), 915; E. Podszus, *Koll. Zeitsch.* **20** (1917), 65.

[4] W. A. Hamer and H. E. Gill, *J. Amer. Ceram. Soc.* **2** (1919), 594.

Certain secondary clays, which contain silica as the main impurity, have a very high softening-point and can be used as "fire-clays." Stourbridge clay is a particularly valuable variety of fire-clay. Most secondary clays, however, contain a comparatively large proportion of fairly fusible constituents. They can often be used as the basis of stoneware, where the body requires to be partly fused, or for pottery. The presence of much iron renders the body produced coloured, and this may limit the use of many of the clays. A large proportion of grains other than mica or kaolin, will clearly reduce the plasticity and may render the material unfit for any use, except, perhaps, for the making of bricks.

Besides clays, other materials are often added to the plastic mixture. They include **felspar** or felspathic rocks, such as the pegmatite known as "**Cornish stone.**" The felspars have a comparatively low melting-point and act as fluxing materials. Calcareous materials like **marl** have also been employed as fluxes. Ground bone-ash (calcium phosphate) is employed in "bone china."

Some form of **silica** (sand, powdered quartz, powdered flint) is often added as an "opening material" to reduce shrinkage, especially in the case of the more plastic clays, which tend to shrink very much. Another excellent "opening material" is *grog*, obtained by crushing disused or broken fired bodies (refractory bricks, crucibles, etc.).

Preliminary Treatment of Clay. The clay as it is dug out at the pit requires to be disintegrated in some way, that is, broken up into fine particles. This may be done mechanically by means of stamping, grinding in ball mills, crushing between rollers, or cutting, but it is possible to allow the forces of Nature to perform at least the first part of the disintegration process. The clay is laid out in small heaps, and allowed to "**weather.**" The evaporation of water by the heat of the sun by day, or the freezing of the water by the frost at night, both serve the same purpose—that of breaking up the clay. It is also thought that artificial weathering serves to convert any residual felspar into kaolin.

Doubt has, however, been expressed as to whether the changes brought about by weathering are actually worth the time and trouble involved in laying out the clay.[1]

The desirability of separating the fine particles of clay from the coarser particles and, as far as possible, from the other minerals that occur with them, will easily be understood. It is, however, only remunerative to treat the best qualities of clays ("China clays," etc.) in this way. Purification is commonly brought about by "washing." The ground or crushed clay is churned up with water in a vat ("blunged"), until the whole of the finer clay particles are in suspension. The water is then allowed to flow out into another vessel, carrying the lighter particles in suspension, whilst the coarser grit remains at the bottom of the "blunger." A further quantity of comparatively coarse material sinks to the bottom in the second vessel, and after a time the water, carrying the finest clay-particles in suspension, is run off. These finest particles are finally separated by settling or by filter-pressing. Any soluble materials remain in the water.

There are, of course, innumerable ways in which the washing and settling process can be elaborated, but the same general principle holds good. It should, however, be noticed that washing will fail to separate the very small particles of foreign substances which can remain suspended as long as the clay particles. For this reason, it seems likely that new processes, based upon the principles of colloid chemistry, may prove more efficient. The simplest process consists in churning the impure clay with water containing an appropriate quantity of alkali, and running the mixture into a settling tank. The kaolin particles adsorb hydroxyl ions, thus assuming a negative charge, and remain suspended as stable colloidal particles indefinitely. The chief impurities (mica, pyrites, silica, etc.) do not adsorb hydroxyl ions so easily, and are uncharged. They consequently sink gradually to the bottom of the tank. The clay-suspension can then be run off from the impurities, and afterwards the kaolin particles can be thrown down by adding a little acid.

The process just described is not entirely satisfactory, but during recent years a promising method of **electrical purification** has been introduced.[2] The apparatus consists of an electrolytic tank, containing the suspension of clay, the anode being a half-immersed cylinder of hard lead, which slowly revolves on a horizontal axis; the cathode is a perforated metal plate, and is fixed just below the anode. Two paddles keep the clay particles in suspension, and direct a continuous stream of the turbid liquid through the perforations in the cathode towards the anode. The negatively charged kaolin particles stick to the anode, whilst the foreign particles (pyrites, mica and quartz), which are neutral or positive, pass out with the effluent from the tank. The process can be made continuous, fresh clay suspension running in by one pipe, whilst a liquid containing impurities (and still a little kaolin) passes off by another. The clay particles adhere to the anode as it rotates, and are removed as a thick *blanket* by scrapers fixed close to the anode surface above the liquid. The blanket of purified clay falls off into a chute clear of the machine.

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[1] L. B. Rainey, *Trans. Amer. Ceram. Soc.* **16** (1914), 405.

[2] J. S. Highfield, W. R. Ormandy and D. Northall-Laurie, *J. Roy. Soc. Arts.* **68** (1920), 514; W. R. Ormandy, *Trans. Ceram. Soc.* **18** (1918-19), 327; *Trans. Faraday Soc.* **16** (1921), Appendix, p. 141; P. H. Prausnitz, *Zeitsch. Elektrochem.* **28** (1922), 32.

The comparative dryness of the blanket obtained may excite surprise, but a little consideration will suggest the reason. The clay particles are negatively electrified relatively to the water; in other words, the water is positively electrified relatively to the clay. The first action of the E.M.F. is to drive the particles on to the anode; having reached the surface they can move no farther, but the water is still free to move in the opposite direction, and is largely expelled from the pores between the clay particles by the same electrical agency. Osmose is therefore not only a purifying process, but also a drying process.

The great importance of the electric " osmose " system is that it has allowed crude clays to be used for purposes to which they have hitherto been found unsuited. For instance, a clay hitherto regarded as only fit for the making of rather low-grade bricks, is now employed—after electric treatment—for making quite good stoneware.

Operations in the Manufacture of Ceramic Articles. Details of the potter's art must be sought elsewhere.[1] It is only possible here to state the stages through which the materials pass.

First the materials (clay and others) are measured out and mixed, the mixture being ground between rollers, or churned up in some other way so as to render the whole uniform. The thoroughly mixed material next undergoes **shaping** to the required form; the method varies, of course, with the nature of the article required. Vases and jars are often " **thrown** " on a potter's wheel, and the shape is sometimes elaborated by " **turning** " on a lathe, a suitable tool being placed against the rotating vessel so as to obtain the desired contour. Plates are sometimes produced by a special form of turning known as " **jiggering** "; a mould representing the shape of the top surface of the plate is mounted on a rotating vertical axis; clay is placed upon it, and a tool having the outline of the plate bottom is lowered to a point just above the surface of the rotating mould, and held practically stationary until the clay has assumed the correct form. Bricks and pipes are **extruded** through a die, the extruded portion being cut off automatically as soon as the desired length has been forced through the aperture. Perhaps the commonest method of shaping an object is to **press** it in a mould; this is used not only for tiles, plates, reliefs, etc., but also for such objects as jugs. In addition, there is the method known as "**slip casting,**" especially suitable for thin china-ware; here a liquid body (or *slip*) is introduced into a porous mould. Part of the water is absorbed into the mould, and a layer of clay-stuff is left all over the interior surface. The excess of liquid is poured away, and the clay in the mould is left to harden.

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[1] See E. Bourry's " Treatise on Ceramic Industries," Translation and critical notes by A. B. Searle (Scott, Greenwood). Also G. Martin's " Industrial Chemistry " (Crosby, Lockwood), Vol. II.

However prepared, the articles are packed in drying stoves where they are gradually **dried,** usually in a current of warm air derived from the kilns. After drying, the goods are often sprayed with a liquid carrying the material which will form the glaze after firing; this matter is considered below.

The articles are next **fired.** Here again the details of the process and the character of kiln employed must vary with the nature of the article to be made. Table-ware (plates, etc.) are packed into boxes (*saggers*), which are then piled in kilns; porcelain, which becomes almost liquid during the firing process, requires very careful packing, with support at points of weakness, since otherwise the articles will lose shape. Stoneware which is to receive salt glaze must be packed so that it comes into direct contact with the hot gases from the fire. Bricks are packed for baking in such a way that the hot gases can get access to each of them.

Coal is commonly used as fuel in this country. On the Continent, producer gas has found application, regenerators being fitted to the furnaces. Heating should generally be slow, and the subsequent cooling must also be slow.

The temperature to be employed will depend on the type of body desired, but also naturally on the composition of the mixture, being lowest where iron and alkali metals are present in considerable quantities. According to Bourry, with high-class materials, the temperature required for faience (superficial fusion or welding of particles) is about 1,200° C., whilst that required for hard porcelain (nearly complete fusion) is about 1,350° C. Builder's bricks, being made of clays rich in fluxes, are fired at a somewhat lower temperature than faience (perhaps 1,000–1,100° C.), although where hard vitrified bricks are to be made, temperatures up to 1,300° C. may be employed. Firebricks and refractory articles require a considerably higher temperature.

The temperature of the kilns is often regulated by means of a series of "*Seger's cones*," which are small slim pointed tetrahedra about 2½ inches high and about ½ inch diameter at the base. Each cone of the series has a standard composition and will soften at a known temperature; the different cones are assigned numbers which indicate their fusibility. The high-temperature cones are mainly composed of china clay; the low-temperature cones contain felspar and other readily fusible substances. A row of cones is placed in the furnace, and by observing which cones droop, and which retain their shape, the furnace-man can obtain a good idea of the temperature.

In addition to this simple, but quite effective, method of gauging the temperature, numerous reliable pyrometers are now available for temperature measurement. Some of these depend upon the use of a thermo-couple, but it is not always necessary to place the pyrometer inside the furnace; a radiation pyrometer has been designed which can be set up outside the furnace, in front of an opening in one wall, and receives heat by radiation from the hot interior surface of the wall opposite. Optical pyrometers, which actually measure the brightness of the white hot walls, have also given good results, although their use introduces some uncertainties.

The first reaction which occurs on heating a ceramic body is the loss of the combined water of the kaolin, probably about 400° C. At much higher temperatures, portions of the body become liquid, the smaller and more impure particles (i.e. particles rich in iron or alkali-metals) being first affected; however, where two large pure particles of different compositions touch one another, mutual "fluxing" may often occur at the point of contact. For instance, a highly siliceous grain and a highly basic grain may fuse together, a comparatively fusible mixture being produced where they touch. As to how far the softening of the mass is allowed to proceed depends upon the material desired, and the various cases must be considered separately.

I. **Refractory Bricks,**[1] **etc.,** consist essentially of some substance with high melting-point (kaolin, silica, magnesia, alumina, chromite, zirconia). It is usual to mix a certain amount of comparatively coarse material, previously calcined ("grog"), with a certain amount of finely powdered material. An agglomerant, such as tar or starch, is used in some cases where the fine material has no natural binding power. A very high temperature is required; the finely divided material softens, and welds the larger grains together. The shrinkage of refractory materials is often serious, both during the drying process and the firing, and care must be taken to secure the correct conditions, or cracking will occur.

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[1] J. W. Mellor, *Trans. Faraday Soc.* 12 (1917), 137. Also numerous other articles on refractories in same volume.

Where the pure material has a very high melting-point, firing is made easier by mixing in a trace of some fluxing substance in a fine state of division. Thus in making silica bricks a little milk of lime is added to the pasty mixture, whilst it is difficult to prepare zirconia bricks without adding some such oxide as alumina or magnesia. In this way the firing is clearly made easier, and the brick prepared is stronger, the particles being cemented together more efficiently; but it is obvious that such an admixture will render the product less refractory.

IIA. **Terra-cotta, Earthenware, Bricks, Faience, etc.** The mixture consists of clay usually mixed with sand, grog, or sometimes powdered flint, as opening agent, to reduce shrinkage. Often, for faience, Cornish stone or felspar is added as a flux; sometimes a calcareous substance, like marl. It is probable that when these articles are properly fired, the smaller and most fusible particles present between the larger grains melt together to form a glass or slag, which, after cooling, cements together the larger particles. Probably the larger particles never become fused except on the surface; the proportion of the matter which becomes fused is actually small, and the mass remains porous after the treatment.

IIB. **Stoneware** may be made by heating a vitrifiable clay (i.e. a clay containing particles rich in iron or other fusible constituents); alternatively it can be made from a mixture of fireclay and felspathic material, such as Cornish stone. The articles are fired at such a high temperature that the greater portion becomes fused, and hardens on cooling to an extremely hard, vitreous ground-mass. Since, however, the more refractory particles (e.g. the silica grains of the clay) have resisted fusion, the ware is far from homogeneous, and is opaque to light. Stoneware is almost non-porous.

IIC. **Porcelain. English bone china** is made from a mixture of china clay, Cornish stone and bone ash; the bone ash acts as a fluxing material. The mixture is heated until nearly the whole of the constituents are in the vitreous condition; an oxidizing atmosphere is needed for the heating, in order to avoid risk of discoloration, and the ovens employed must be designed accordingly.[1] Bone china is almost the only kind of soft porcelain made in this country. **Continental soft porcelains**, however, do not contain bone ash; some varieties consist of the same constituents as hard porcelain (see below), although in different proportions; there is, for instance, less china clay.

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[1] S. T. Wilson, *Trans. Ceram. Soc.* **16** (1917), 304.

On the Continent, **hard porcelain** is made more commonly than soft, being prepared from mixtures containing kaolin, felspar, and quartz. Here again almost the whole of the constituents undergo alteration during the process of firing; the felspar fuses, and attacks the quartz, whilst the kaolin loses water in the earlier stages of heating, yielding a vitreous mass, from which minute needle-shaped crystals of sillimanite, $Al_2O_3.SiO_2$, separate at a high temperature.

Both kinds of porcelain are translucent and vitreous after firing, but they are not absolutely homogeneous and transparent like true glass. This is partly because some of the original particles escape vitrification; even in the best porcelain some of the large quartz grains remain unattacked, and in the less choice varieties there is still less dissolution of this refractory constituent. The lack of transparency may also be due to the appearance of fresh crystals, e.g. those of sillimanite, during burning; such crystals can usually be seen in microphotographs of sections of hard porcelain.[1]

English bone china gives less trouble in saggering than does hard porcelain, and it is comparatively easy to obtain any colour desired upon the former, whereas with hard porcelain there are difficulties in obtaining certain colours. Bone china is also rather less brittle than most kinds of hard porcelain.

Glazes. It is very usual to cover ceramic articles with a "glaze" or thin layer of glass. In the case of earthenware, pottery, etc., where the body is porous, the glaze serves to make the article impervious and water-tight. In addition, a non-transparent glaze, containing substances of high refractive index like tin compounds, serves to conceal the unattractive colour of the body. In stoneware and porcelain, which have non-porous bodies, the glaze serves mainly to improve the appearance of the article, although it should be added that certain types of so-called stoneware are very perceptibly porous, and, in such cases, the glaze fulfils a most necessary function in rendering the articles water-tight.

Essentially the glaze formed upon the surface of an article is, like ordinary glass, a mixture of silicates, but borates are sometimes present, being added to make the mixture more fusible and to increase the hardness and brilliance. The basic oxides present may include oxides of calcium, potassium, sodium, lead and aluminium. For non-transparent glazes an opacifier, such as oxide of tin or oxide of antimony, should be present, which remains in suspension in the glaze. Alumina, calcium phosphate, zinc oxide and titanium oxide have also been used as opacifiers.

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[1] A. A. Klein, *U.S. Bur. Stand.*, Technical Paper **80** (1916); *J. Franklin Inst.* **182** (1916), 683; *J. Amer. Ceram. Soc.* **3** (1920), 998. Microphotos of bone china, after firing at different temperatures, are given by J. W. Mellor, *Trans. Ceram. Soc.* **5** (1905), 80.

As a rule, a *frit* is made by melting together appropriate quantities of the chosen materials in a crucible or small reverberatory furnace. A lead silicate frit can be made by fusing together quartz sand, boracic acid, lead oxide (usually red lead), chalk, and a small quantity of clay. Sometimes soda ash and felspar are also present, and in " leadless glazes " these substances containing alkali metals take the place of the lead compounds altogether ; in leadless glazes, the boracic acid content must be increased, or the glaze will be too infusible.

Where a non-transparent glaze is needed, tin oxide is added, and this may also reduce the fusibility and call for an increase in the boracic acid content.

After the preparation of the " frit," it is finely ground with water, so as to obtain a fine suspension ; often other substances, such as finely powdered felspar are added to the suspension. The suspension is generally applied to the articles after drying and before firing, but sometimes—as in the case of porcelain—to the article (" biscuit ") after the first firing ; in such cases, a second firing is needed after the application. The suspension is usually applied by spraying, although sometimes the articles are dipped into the liquid. During the subsequent firing, the particles of the frit melt again and spread as a glassy layer over the whole surface, penetrating into any pores, and often reacting or blending with the material of the body. In hard porcelain it is impossible to say definitely where the body ends and the glaze begins. The composition of the glaze should in all cases be chosen to suit the body ; the coefficient of expansion of the two should, for instance, be roughly the same, because, if the glaze contracts more than the body when the article is cooled, it may crack (this is known as *crazing*), whilst, if it contracts less, it may become detached (*scaling* or *peeling*). Crazing is likely to occur when the glaze contains too little silica, scaling when it contains too much.

The danger of lead-poisoning through the use of lead glazes has been greatly reduced in recent years by the more careful regulation of the process, and particularly by the application of the lead in the form of " frit " (silicate), instead of as white lead (basic carbonate) or red lead (oxide), as was formerly the case. This has been the main factor in reducing the cases of " plumbism " in the pottery trade of this country from 200 in the year 1900 to only eleven in 1918.[1]

The composition of the frit must clearly be such that the lead (or alkali metals) in it are not unduly soluble in the water in which they are suspended during application.[2]

The well-known "salt glaze" often seen on stoneware articles is obtained in an entirely different way. Sodium chloride is thrown directly into the fire of the furnace, or sometimes placed in the hot part of the kiln (not directly on the articles). The salt vaporizes at once, and the vapour interacts with the silicates of the surface of the body, producing upon the surface a comparatively fusible silicate mixture containing sodium silicate, which on cooling hardens to a transparent glassy layer.

Colour of Ceramic Materials. The colour of the body is seldom white, unless the materials used are singularly free from iron. Even in bone china, which is made from the purest china clay, with only a trace of iron, a coloration (due to iron phosphates) appears if the proportion of bone ash, Cornish stone and china clay are not quite right, or if the articles are fired in a reducing atmosphere or at the wrong temperature.[3] In earthenware, where less pure materials are used, the colour of the body is never white, but if the articles are glazed with a non-transparent glaze, the colour is hidden. In some cases, a white layer (a "slip" or "engobe") made of pure materials (china clay, etc.) is applied to the surface of the coloured body, and the article is subsequently glazed. In unglazed articles, like bricks, or in articles with a transparent glaze, like salted stoneware, the colour of the body becomes noticeable. Bricks, for instance, vary very much in colour. The yellow colour of common bricks is due to a finely divided modification of ferric oxide, which is stable in presence of alumina. If agglomeration of the ferric oxide particles occurs, a red brick is produced. The presence of lime in the bricks favours the retention of the yellow colour, whilst excess of iron tends to cause a red brick.[4] Burning at a high temperature, especially in the presence of reducing substances, yields a dark-red, black or blue brick, largely vitrified. The dark colour has been ascribed to carbon, but is generally due to the magnetic oxide of iron (Fe_3O_4), or a corresponding ferroso-ferric silicate.

For decorative purposes, faience and porcelain articles are often coloured by introducing small quantities of those metallic oxides which confer coloration upon silicate glasses. The colour may be applied in five ways :—

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[1] S. Miall, *J. Soc. Chem. Ind.* **39** (1920), 4R.

[2] L. Petrik, *Sprechsaal*, **53** (1920), 405.

[3] J. W. Mellor, *Trans. Ceram. Soc.* **18** (1918–19), 497.

[4] I. A. Keane, *J. Phys. Chem.* **20** (1916), 734; F. H. Scheetz, *J. Phys. Chem.* **21** (1917), 570; C. F. Binns, *8th. Int. Cong. App. Chem.* (1912), Sect III c, 7.

(1) The *body* may be coloured, being covered with a transparent glaze, or left unglazed.

(2) A coloured *slip* or engobe may be applied.

(3) The colour may be applied to the surface of the body before the application of the glaze. Afterwards a transparent glaze is applied, into which the colour passes on heating (*underglaze* colouring).

(4) A *coloured glaze* may be used.

or (5) The colour may be applied over the glaze, usually after burning, by means of a mixture which can vitrify by subsequent heating at a low temperature (*overglaze* colouring). The vitrifiable mixture often consists of lead borate and silicate ; bismuth compounds are sometimes added to increase the fusibility.

In the last method, colours can be used which would not stand the temperature of the firing proper. If one of the other four methods is applied, the colour will often depend upon the temperature of firing and on the general composition of the body, slip or glaze, as well as on the oxidizing or reducing character of the atmosphere in the kiln. Subject to these qualifications, the following short list indicates some typical methods of obtaining the different colours :—

Black, by mixtures of iron and chromium oxides ; or iron and cobalt oxides.

Deep Blue, by cobalt oxides (must not be burnt in reducing atmosphere).

Turquoise Blue, by copper oxide in oxidizing atmosphere (difficult to apply to hard porcelain).

Green, by chromium oxides.

Yellow, by a mixture of antimony and lead oxides ; or by titanium and zinc oxides ; or by uranium. Chromic acid gives a yellow in alkaline glazes.

Red. Zinc oxide with a trace of chromic acid in an oxidizing atmosphere gives a red ; also iron oxide under certain circumstances. Fine ruby reds are obtained with colloidal gold (Purple of Cassius), or with copper.

Violet, by manganese in alkaline glazes.

Gold, by metallic gold applied above the glaze, in finely divided form. (It should be burnished after burning.)

Many other mixtures of oxides are also used extensively.

Where underglaze or overglaze decoration is required, the colouring matter or the vitrifiable mixture is sometimes applied by hand, the finely powdered materials being mixed with gum, turpentine or glycerine, and painted on with a brush. More often mechanical methods of applying the colour are employed. In the subsequent firing, especial care must be taken to control the temperature, and also the type of atmosphere in the furnace.

THE RARE-EARTH METALS

		Atomic Weight.	Atomic Number.
GROUP IIIA	Scandium	45·1	21
	Yttrium	89·33	39
	Lanthanum	139·0	57
GROUP IVA	(Cerium)	140·25	58
CERIUM FAMILY	Praseodymium	140·9	59
	Neodymium	144·3	60
	Unknown element	—	61
	Samarium	150·4	62
	Europium	152·0	63
	Gadolinium	157·3	64
YTTRIUM FAMILY	Terbium	159·2	65
	Dysprosium	162·5	66
	Holmium	163·5	67
	Erbium	167·7	68
	Thulium	168·5	69
	Ytterbium (Neo-ytterbium)	173·5	70
	Lutecium	175·0 (?)	71
GROUP IVA	*Unknown element* (probably Hafnium)	180·0 (?)	72

General

The three heavier metals of Group IIIA, scandium, yttrium and lanthanum, resemble each other very closely; it is natural, therefore, to consider them together. But it is necessary to describe at the same time a large number of other elements, which have very similar properties. Nearly all the elements which fall, in the order of atomic weights, between lanthanum (atomic weight 139·0) and tantalum (atomic weight 181·5) form compounds in which the metals are trivalent. The character of these compounds would lead us to place the elements in Group IIIA, although if the orderly sequence of the Periodic Table were to persist, they should fall in other groups; we should, for instance, expect cerium (atomic weight 140·25) to fall into Group IVA, praseodymium (140·9) to fall into Group VA, neodymium (144·3) into Group VIA, and so on. The properties of the metals, however, are not such as would justify that arrangement. Cerium, it is true, has a class of compounds (in which the metal is tetravalent) closely related to the compounds of zirconium and thorium; indeed, cerium forms, in some respects, a link between zirconium and thorium, and for this reason is placed by many chemists in Group IVA. On the other hand, the more characteristic compounds of cerium are those in which the metal is trivalent; these closely resemble the compounds of lanthanum. Whatever arguments may be adduced in favour of placing cerium in Group IVA, there is very little to justify us in assigning to praseodymium and neodymium the vacant places in Groups VA and VIA. Praseodymium has but little in common with niobium and tantalum, and neodymium has even less in common with molybdenum and tungsten. On the other hand, the characteristic compounds of praseodymium and neodymium are so similar to those of lanthanum that the two metals can only be separated from lanthanum with difficulty. The same may be said of the remaining rare-earth metals. Any attempt to distribute them over the various groups of the Periodic Table ends in failure. The properties of the elements do not, in general, correspond to those of any group except Group IIIA. In every case, the stable compounds are those corresponding to the oxide of the type M_2O_3, although in a few cases other compounds do exist. Praseodymium and neodymium, for instance, have higher oxides PrO_2,NdO_2, whilst in samarium there is actually a class of lower salts ($SmCl_2$, etc.). In cerium, as has been stated, there are fairly stable salts corresponding to the oxide CeO_2, and these salts are similar to the salts of zirconium and thorium. For this reason cerium will be discussed in detail along with the tetravalent metals of Group IVA.

The occurrence of the rare earth metals in the middle of the Periodic Table appears at first sight to be a break in the orderly sequence of the elements, and it is certainly a little difficult to reconcile their existence with the old notion of the periodic recurrence of properties in the elements. It is necessary to place them in a group by themselves in the centre of the Periodic Table, and to regard the orderly sequence of the elements as being suspended between lanthanum and tantalum. It is remarkable that at tantalum the sequence recommences; tantalum has all the properties of an element of Group VA, and the succeeding element, tungsten, clearly belongs to Group VIA. Apart from the fact that the next element (which should belong to Group VIIA) appears to be undiscovered, every succeeding element has exactly the properties which its place in the Periodic Table would seem to indicate, and no further "failure" of the table occurs until uranium, the last of the elements, is reached.

It is clearly necessary to abandon the old idea, which still survives in the minds of many chemists—presumably because the old-fashioned eight-column form of the Periodic Table still hangs upon the walls of our lecture-rooms—that the properties of the elements recur regularly *every eight elements.* It is necessary to consider afresh the experimentally proved facts in a spirit free from prejudice or convention. If this is done, the interpolation of the large rare earth group of elements is found, not to be a departure from the sequence of the elements, but to be entirely consistent with it.

Whatever form of the Periodic Table is adopted, the inert gases (helium, neon, argon, krypton, xenon and niton), must clearly be considered to constitute a natural group. If we define a "period," as the series of elements occurring between one inert gas and the next, we can—as was pointed out by Harkins[1]—express the sequence of the elements in an orderly fashion, as follows :—

(*a*)	*Very Short* Period ending in Helium .	2 Elements, i.e. 2×1^2
(*b*)	First *Short* Period ending in Neon . .	8 Elements, i.e. 2×2^2
(*c*)	Second *Short* Period ending in Argon .	8 Elements, i.e. 2×2^2
(*d*)	First *Long* Period ending in Krypton .	18 Elements, i.e. 2×3^2
(*e*)	Second *Long* Period ending in Xenon .	18 Elements, i.e. 2×3^2
(*f*)	First *Very Long* Period ending in Niton	32 Elements, i.e. 2×4^2
(*g*)	Second *Very Long* Period. Incomplete.	—

In stating that the number of elements in the first *very long* period was thirty-two, Harkins assumed that there were exactly sixteen rare earth elements (including lanthanum) in the space between lanthanum and tantalum. If we are to accept Harkins's view of the periodic classification, we have to adopt the idea that two, and only two, rare-earth elements remain undiscovered.[2] This is a most important point; for the different rare earth elements occur in nature mixed together, and in very small quantities, and, being very similar in properties, are difficult to separate from one another. Consequently, only a few decades ago, it seemed an almost hopeless task to decide how many of these elements remained undiscovered. Repeatedly, in the history of the rare earths, it has happened that a preparation, believed to be a salt or oxide of a single metal, has been found, on careful fractionation, to be a mixture of two salts or oxides. Harkins's generalization, if accepted, would fix the total number of these earths definitely at sixteen, and limits the number of undiscovered members to two.[3]

Convincing evidence that the number of the rare earths is exactly sixteen is afforded by the X-ray emission spectra of the elements of higher atomic numbers.[1] If the number of rare-earth elements is sixteen, the atomic number of lanthanum being fifty-seven, it follows that the atomic number of tantalum is

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[1] W. D. Harkins and R. E. Hall, *J. Amer. Chem. Soc.* 38 (1916), 169.

[2] The discovery of *hafnium*, if accepted, reduces the number to one.

[3] See also R. Vogel, *Zeitsch. Anorg. Chem.* 102 (1918), 177. Vogel differs from Langmuir regarding the position of the second undiscovered element. (Caution.—There are two misprints in the table on p. 194 of Vogel's paper.)

$$57 + 16 = 73,$$

whilst the atomic numbers of succeeding elements will be

Tungsten	74
Undiscovered element in Group VIIA	75
Osmium	76
Iridium	77
Platinum	78
Gold	79

Now the X-ray emission spectra of these elements is known, and accords with the values of the atomic numbers just given. On the other hand, if the number of rare-earth elements exceeded sixteen, the atomic numbers of the various elements would exceed the values suggested, and this would be inconsistent with the wave-length of the emitted X-rays as experimentally determined. Moreover, the X-ray spectra of many of the rare-earth metals have been studied by Moseley, and are found to be consistent with the atomic numbers assigned to them at the commencement of this section. The position of the lighter of the two missing elements is placed—as a result of Moseley's work—between neodymium and samarium.

Harkins's estimate of thirty-two for the number of elements in his first *very long period* may fairly be accepted. A simple physical explanation for the occurrence in succeeding periods of

2, 8, 8, 18, 18 and 32 elements

is suggested by Langmuir's theory of the atom.[2] Langmuir has shown that, if the outermost electrons of the atoms are assumed—

in the elements of the *very short* period to be situated on a spherical shell of radius r,
in those of the *short* periods to be situated on a spherical shell of radius $2r$,
in those of the *long* periods to be situated on a spherical shell of radius $3r$,
and in those of the *very long* periods to be situated on a spherical shell of radius $4r$,

and if, in each of the inert gases (in which the outer shell is complete and perfectly stable) the same area is assigned to each electron in each shell, then geometrical considerations demand that the number of elements in each period must be the numbers stated above. For further details of this theory, the original paper must be consulted.

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[1] H. G. J. Moseley, *Phil. Mag.* **27** (1914), 703.
[2] I. Langmuir, *J. Amer. Chem. Soc.* **41** (1919), 868.

Bohr's theory of the atom is also able to account for some of the facts regarding the interpolation of the rare-earth group in the Periodic Scheme. It affords an explanation of the remarkable similarity of the elements to one another. It is impossible to summarize the argument here, and Bohr's paper should be referred to.[1]

If the sixteen rare-earth elements are written in order of atomic weights, gaps being left for the two missing elements, and a new line being commenced after the eighth element, we seem to get a natural classification, thus :—

CERIUM FAMILY	57 La	58 Ce	59 Pr	60 Nd	61 —	62 m	63 Eu	64 Gd
YTTRIUM FAMILY	65 Tb	66 Dy	67 Ho	68 Er	69 Tu	70 Yb	71 Lu	— —

The first row consists of the so-called *cerium family*, having insoluble double potassium sulphates ; the second row consists of the *yttrium family* with soluble double sulphates. In each row, the elements with distinctly coloured compounds occur near the centre ; the salts of metals at each end of the row have their absorption bands mainly outside the visible part of the spectrum and there is little or no colour. The fact that two metals with rose-coloured salts—neodymium and erbium—fall one below the other, is worthy of note, although it may be purely fortuitous.

Chemistry of the Rare-earth Elements. Owing to the rarity of the metals under discussion, the chemistry of their compounds has not been fully investigated. In some cases, the metal itself has never been prepared, and only those properties of the salts which are useful in separating one element from another have been studied in any detail.

Owing to the general similarity of properties, a separate discussion of each element would involve much repetition. Consequently, the more important peculiarities of each individual element are given in tabular form below, followed by a short generalized description of the chemistry of the group as a whole.

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[1] N. Bohr, *Zeitsch. Phys.* 9 (1922), 1 ; especially page 54.

Element.		Melting Point. C.	Oxides.		Colour of Salt (in solution).		Solubility of Double Sulphate in K_2SO_4 or Na_2SO_4 solution.
Scandium			Sc_2O_3	White	$Sc^{\cdot\cdot\cdot}$	colourless	Soluble in Na_2SO_4 Less soluble in K_2SO_4
Yttrium	Dark-grey		Y_2O_3	White	$Y^{\cdot\cdot\cdot}$	colourless	Soluble
Lanthanum	Iron-grey	810°	La_2O_3	White	$La^{\cdot\cdot\cdot}$	colourless	Insoluble
			Ce_2O_3	Yellow-green			
Cerium	Iron-grey	623°	Ce_4O_7	Blue	$Ce^{\cdot\cdot\cdot}$	colourless	Insoluble
			CeO_2	White or yellow	$Ce^{\cdot\cdot\cdot\cdot}$	yellow	
Praseodymium	Yellow	940°	Pr_2O_3	Green	$Pr^{\cdot\cdot\cdot}$	green	Insoluble
			PrO_2	Black			
Neodymium	Yellow	840°	Nd_2O_3	Blue	$Nd^{\cdot\cdot\cdot}$	rose	Insoluble
			NdO_2	(?)			
(Unknown element here)							
Samarium	White-grey	1,350°	Sm_2O_3	Yellowish	$Sm^{\cdot\cdot\cdot}$	yellow	Insoluble
					($Sm^{\cdot\cdot}$	red-brown)	
Europium			Eu_2O_3	White with pink tinge	$Eu^{\cdot\cdot\cdot}$	pink	Insoluble
Gadolinium			Gd_2O_3	White	$Gd^{\cdot\cdot\cdot}$	colourless	Moderately insoluble
Terbium			Tb_2O_3	White	$Tb^{\cdot\cdot\cdot}$	practically colourless (one absorption band in blue)	Soluble
			Tb_4O_7	(?) Brown or black			
Dysprosium			Dy_2O_3	White	$Dy^{\cdot\cdot\cdot}$	green	Soluble
Holmium			Ho_2O_3	Pale yellow	$Ho^{\cdot\cdot\cdot}$	yellowish	Soluble
Erbium			Er_2O_3	Rose	$Er^{\cdot\cdot\cdot}$	rose	Soluble
Thulium			Tu_2O_3	White, faint green tinge	$Tu^{\cdot\cdot\cdot}$	green	Soluble
(Neo-) Ytterbium			Yb_2O_3	White	$Yb^{\cdot\cdot\cdot}$	colourless	Soluble
Lutecium			Lu_2O_3	(?)	$Lu^{\cdot\cdot\cdot}$	colourless	Soluble

The Metals

The metals, in such cases as they have been prepared, are grey or yellow bodies, fusing at moderate temperatures. They seem to be highly reactive, falling between zinc and magnesium in the potential series, the probable order being

$$\mathrm{Zn,\ Ce,\ La,\ {Nd \atop Pr},\ Mg.}$$

Their position, therefore, is comparable to that of aluminium, but, in the case of the rare-earth metals, the reactive character of the element is only to a small extent modified by the presence of a protective oxide film. In consequence, the metals for the most part slowly decompose water, hydrogen being evolved. The hydroxide produced hinders, but does not put a stop to, the reaction. With dilute acids, hydrogen is evolved very readily, the salts being produced. The metals burn when heated in air, and tend to oxidize at ordinary temperatures. Most of the metals yield pyrophoric materials when alloyed with iron; that is to say, the alloys give off white-hot, luminous sparks when filed or scraped, owing to the rapid oxidation of the fragments of metal that fly off. But in most cases, the pure metals are not pyrophoric, probably because they are too soft to give off the necessary splinters when filed.[1]

Some of the metals, notably gadolinium, terbium and dysprosium, are strongly paramagnetic.[2] In this, and certain other respects, the rare-earth metals seem to be allied to the "transition elements" (iron, nickel, cobalt, etc.) which stand in the centre of the Periodic Table.

The preparation of the metals is most easily brought about by the electrolysis of the fused chlorides. The electrolysis may be carried out in a graphite crucible, which forms the cathode. To minimize the absorption of carbon by the metal, it is beneficial to cover the sides of the crucible with a layer of alundum cement, leaving the bottom bare.[3] The presence of moisture in the bath is very prejudicial to the yield, and great care must be taken that damp air has no access to the electrolyte. The anhydrous chloride is best obtained by heating the hydrated chloride with ammonium chloride.

In some cases, the metal is more easily prepared by the action of sodium on the fused chloride, heated *in vacuo*.

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[1] B. Weiss, *Zeitsch. Elektrochem.* **14** (1908), 549.

[2] B. Urbain and G. Jantsch, *Comptes Rend.* **147** (1908), 1286. Compare E. Wedekind, *Ber.* **54** (1921), 253.

[3] J. F. G. Hicks, *J. Amer. Chem. Soc.* **40** (1918), 1619.

Compounds

The **oxides** (M_2O_3) or *earths* (popularly known as "*lanthana*," "*yttria*," etc.) are formed, of course, when the metals are heated in oxygen. They are in most cases conveniently obtained by heating the nitrate or oxalate. The **hydroxides** are thrown down as gelatinous precipitates when ammonia or caustic soda is added to the solution of the salts, in the presence of ammonium chloride, and are usually of the same colour as the salt solutions. They differ from aluminium hydroxide in being insoluble in alkalis. When heated they yield the oxide. **Higher oxides** are known in the case of a few of the metals, being obtained by heating the nitrate or oxalate in air. By heating praseodymium nitrate with nitre, a blackish oxide (PdO_2) is obtained [1]; neodymium also forms a higher oxide. When terbium oxalate is heated, a red-brown body of rather variable composition is produced, to which the formula Tb_4O_7 has been assigned.[2]

The **Salts** are mostly soluble compounds, which are colourless in some cases, but are rose, green and yellow in others; the absorption bands are in most cases characteristic, and serve for the detection and distinction of the metals. The appearance of colour is another fact which suggests that the rare-earth elements are related to metals standing in the centre of the Periodic Table. The **chlorides, sulphates** and **nitrates** are soluble crystalline solids; the anhydrous chlorides have a considerable affinity for water, but differ from aluminium chloride in being comparatively non-volatile. The **carbonates** and **oxalates** are insoluble and are obtained by precipitation.

The **sulphides** can in some cases be obtained most easily by the action of carbon disulphide on the oxide. Lanthanum and praseodymium sulphides are prepared by the action of hydrogen sulphide gas on the dry sulphate. They cannot be prepared by precipitation from aqueous solution. In both these cases, besides the normal sulphides, La_2S_3 and Pr_2S_3, disulphides LaS_2 and PrS_2, are known.[3]

Most of the metals form yellowish **nitrides** (of general formula MN) which yield ammonia when treated with water.

Several of the metals form double sulphates with potassium, which are almost insoluble in strong solutions of potassium sulphate. Trivalent cerium behaves in this way. If a solution of cerous sulphate, $Ce_2(SO_4)_3$, is treated with excess of potassium sulphate, practically the whole of the cerium is precipitated as the double salt $3K_2SO_4.Ce_2(SO_4)_3$ or $K_3[Ce(SO_4)_3]$. Analogous insoluble double sulphates are formed in the case of all the known elements with atomic numbers between 57 and 64, namely lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium. The other metals of the group, namely the elements with atomic numbers between 65 and 72—as well as yttrium—are not precipitated by potassium sulphate in this way. This fact is of extreme importance, because it enables us to divide the metals into the two natural families which have already been referred to :—

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[1] B. Brauner, *Proc. Chem. Soc.* **14** (1898), 70; **17** (1901), 66.

[2] G. Urbain, *Comptes Rend.* **141** (1905), 521.

[3] W. Biltz, *Zeitsch. Anorg. Chem.* **71** (1911), 427.

(1) the *Cerium family*, which is precipitated by potassium sulphate :—

La, Ce, Pr, Nd, Sm, Eu, Gd.

and (2) the *Yttrium family*, which is not precipitated :—

Sc, Y, Tb, Dy, Ho, Er, Yb, Lu.

It should be mentioned that both gadolinium and scandium lie somewhat on the border-line between the two groups ; gadolinium is largely precipitated along with the cerium family but partly appears in the filtrate along with the yttrium earths. Scandium is, to a considerable extent, precipitated by potassium sulphate, but is not precipitated by sodium sulphate.

Analytical

The rare earths are precipitated under the same conditions as aluminium, namely by ammonia in the presence of ammonium chloride. They can be separated from aluminium, iron and chromium, by precipitation with oxalic acid in weakly acid solution. Oxalates of the rare earths are insoluble in acids and are thrown down under these conditions, the other metals mentioned remaining in solution. Oxalates of thorium and zirconium may also be precipitated under these circumstances, but can be largely removed by boiling the precipitate with ammonium oxalate solution, which dissolves zirconium and most of the thorium.

The rare earth metals can thus be separated quantitatively from other metals (except thorium) in this comparatively simple manner. They can also be separated into the cerium and yttrium families more or less completely by precipitation of the sulphates with potassium (or sodium) sulphate. There is, however, no satisfactory method of carrying the separation any further. If a knowledge of the amount of the individual metals present in a mixture is desired, it is necessary to apply the laborious methods of separation discussed below in the section headed "Isolation of rare-earth metals from mineral sources," endeavouring, by preserving all the fractions of the material, to render the ultimate separation complete and quantitative. This is, as a matter of fact, very nearly impossible.

In certain cases a rough idea of the amount of the coloured elements present can be obtained by the study of the absorption spectra of the salts.

TERRESTRIAL OCCURRENCE

The small quantities of rare-earth elements present in rock magma tend to accumulate in the liquid portion during the process of consolidation, and are to be found in the minerals connected with the final stage of the process. Cerium, and the metals of the cerium family, occurs in notable quantities in certain granites, and in the sands and gravels which have been formed by the weathering of those granites. For instance, the mineral

Monazite, *usually written* (Ce,La,Pr)PO_4, *but containing also thorium,*

occurs in certain sands found in Brazil, India, Ceylon, and elsewhere; these sands are eagerly sought after as sources of thorium. Other important thorium ores, like thorianite, contain cerium. In addition, the hydrated silicate

Cerite[1] . . . $Ce_2SiO_4.xH_2O$

occurs in gneiss in Sweden; besides cerium, it contains about 7 per cent. of lanthanum, praseodymium, neodymium and samarium.

The yttrium metals have a similar mode of origin, and appear to have been evolved, in part, along with the vapours given off during the final stage of consolidation of an intrusive mass. The silicate, which has been mentioned in the section on beryllium,

Gadolinite . . . $Be_2Fe(YO)_2(SiO_4)_2$

occurs in pegmatites. It contains, besides yttrium, the other elements of the yttrium family.

Many other minerals contain the rare earths, especially the complex niobates:—

Samarskite . . A complex niobate and tantalate of iron, calcium and the rare-earth metals.
Euxenite . . . A complex niobate and titanate of the rare earths and uranium.

Moreover traces of rare-earth metals occur in many common minerals, and are occasionally the cause of coloration. Certain specimens of apatite have a red-violet colour, commonly attributed to manganese, but really due to neodymium.[1] Yttrium is a particularly widely distributed element.[2] Minerals like strontianite, witherite and aragonite often contain 0·05 to 0·2 per cent. of yttrium. One specimen of pink coral was found to contain 0·5 per cent.

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[1] The formula is that suggested by Crookes, who adds, "the true composition of the mineral is only known approximately, and in its structure it is anything but homogeneous."

Scandium, and several other rare-earth elements, occur in small quantities in certain tungsten ores found in Saxony. The silicate of scandium, known as

Thorveitite . . . . $Sc_2Si_2O_7$,

deserves mention, in spite of its rarity, because it is a convenient source of scandium.[3] It is found in certain Norwegian pegmatites and also in Madagascar. Thorveitite contains small quantities of yttrium and ytterbium, but is nearly free from the members of the cerium family.

ISOLATION OF RARE EARTHS FROM MINERAL SOURCES

It is fortunately not necessary for any technical purposes to carry out the complete separation of the various rare-earth minerals. Crude cerium oxide, containing oxides of other rare-earth metals, is obtained as a bye-product of the thorium industry. The mixed oxides are reduced to the metallic state, the product obtained being known as *mischmetall*. It contains most of the rare elements in varying proportions. Mischmetall is alloyed with iron, yielding a pyrophoric material which is used in the manufacture of " flints " for pocket cigarette-lighters and similar purposes. This matter, and other special uses of cerium, will be considered further at a later stage (page 267).

Apart from cerium, the only rare-earth metals which have any technical employment are praseodymium and neodymium. A mixture of the oxides of these two metals (known as *didymia*) is utilized for the production of the pink lettering that may be seen on gas-mantles.

The ultimate separation of the different rare-earth elements[4] has, therefore, been carried out mainly as a matter of research. The details of the method naturally depend on the mineral chosen as the source, and upon the nature of the other metals present in it. Silicates may be decomposed with acid if reduced to sufficiently fine powder. Sulphuric acid brings about the decomposition most quickly in some cases, hydrochloric acid in others, whilst the niobate-tantalate minerals dissolve best in hydrofluoric acid. Fusion with potassium bisulphate has also found application. The residue, after evaporation to dryness, is extracted with water and filtered from silica. From the neutralized solution, most of the foreign metals can be precipitated by ammonium sulphide, and the filtrate from this operation contains the rare-earth metals, including cerium. It is best to precipitate them all together as the insoluble oxalates by adding oxalic acid to the faintly acidified solution. Should thorium and zirconium be present, the oxalate precipitate should be boiled with ammonium oxalate to dissolve out these metals. The insoluble oxalates of the rare earths are then converted to the sulphates by heating with strong sulphuric acid, and the hydroxides can be obtained by precipitation with alkali.

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[1] E. T. Wherry, *J. Wash. Acad. Sci.* 7 (1917), 143.

[2] Sir W. Crookes, *Phil. Trans.* 174 (1883), 891.

[3] P. and G. Urbain, *Comptes Rend.* 174 (1922), 1310.

[4] See C. James, *J. Amer. Chem. Soc.* 30 (1908), 979, for a complete scheme of separation.

In many cases it may be found convenient to use the "earthy residue" obtained in the technical extraction of thoria from monazite as the starting-point for the preparation of individual rare-earth metals.

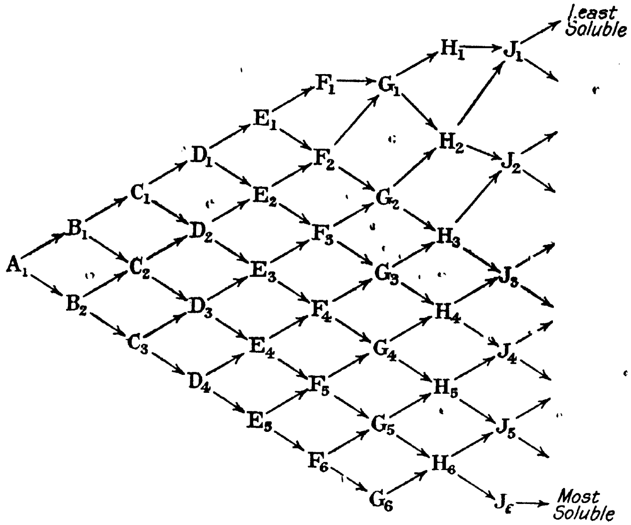
It is possible at once to separate the members of the cerium family from those of the yttrium family by precipitation of the sulphate solution with excess of potassium sulphate or sodium sulphate. The cerium family, it will be remembered, form insoluble double sulphates of the type $M_2(SO_4)_3.3K_2SO_4$, and can thus be removed by filtration; the yttrium family are found in the filtrate.

It is also a simple matter to separate cerium from the other metals belonging to the cerium family, by taking advantage of the fact that cerium forms a higher oxide with very feeble basic properties. The mixed hydroxides are dissolved in nitric acid, and stirred with excess of zinc oxide and potassium permanganate. The cerium is oxidized to the ceric state, and is at once precipitated by the zinc oxide; the other metals remain in solution in the trivalent condition.

But, having divided the metals into the two main classes, the further separation becomes most tedious and difficult. No method is known by which any two of the metals can be separated in a single operation. All that can be done is to apply some such process as fractional crystallization or fractional precipitation, in order to separate the material into different portions respectively richer and poorer in some one metal, the richer fractions being treated again in the same way. By repeating the operation sufficiently often, a comparatively pure compound of the metal in question can finally be obtained. The difficulty of the process is not merely due to the similarity in chemical properties of the different metals, but also to the fact that it is very hard to tell, at the end of the operation of fractional crystallization, what progress—if any—has been made in concentrating the desired metal in certain fractions. Where the metals form coloured salts with characteristic *absorption spectra*, the spectroscope can be used to estimate roughly the amounts of the various metals in different fractions, and the work is greatly facilitated. In other cases, the *spark spectra*, or the *phosphorescence spectra*, have been used as a guide to enable the chemist to "follow" the progress of separation. In general, the pure substances are not phosphorescent, but a very small quantity of a second rare-earth element is sufficient for phosphorescence. The phosphorescence of a rare-earth mixture is conveniently excited by allowing cathode rays to play upon the preparation. More recently it has become customary to study the *magnetic properties* of the fractions, using the results to estimate the approximate quantities of the different earths in the various fractions.

Where one of these methods can be adopted, the chemist who is endeavouring to effect a separation of the different rare metals is not working completely in the dark. But unless some physical method of the kind can be found to guide the chemist, the only method is to determine the average atomic weight of all the different fractions obtained after a series of fractionations—obviously a most tedious process.

The details of a process of repeated fractionation cannot be described in this book, but some idea must be given of the system employed. Suppose that we start with a crude mixture of salts (shown as A_1 in the table below) and desire to employ fractional crystallization to separate it into its more soluble and less soluble constituents. It is dissolved in hot water, and the solution is concentrated and cooled so as to allow about half the salt to crystallize. The mother liquor B_2, containing an increased quantity of the more soluble constituent, is poured off from the crystallized fraction, B_1, in which the less soluble constituent has become concentrated. Each of these fractions are then crystallized a second time, so as to yield two portions; but the most soluble portion from B_1 is mixed with the less soluble portion from B_2. Thus we get three fractions in all, C_1, C_2 and C_3. Each of these is crystallized afresh, and thus the process continues as indicated in the table below. If, after a time, the "most soluble" and "least soluble" fractions of the whole series become inconveniently small, the system may be modified somewhat; for instance the "head" and "tail" fractions may only be fractionated at every alternate stage; when this modified procedure is adopted, the total number of fractions ceases to increase, but the least soluble constituent gradually becomes concentrated in the portions near the "head" of the series, and the most soluble in the portions near the "tail." Obviously it may be convenient to modify the system in many ways to suit the requirements of individual cases, but the same general principles usually apply. Fractional precipitation is also conducted in a methodical manner, based upon rather similar principles to those employed in fractional crystallization.



Separation of the Metals of the Cerium Family

Cerium itself is comparatively easily separated, as described above, owing to the weak basicity of ceric oxide. This leaves the nitrates of lanthanum, praseodymium, neodymium, samarium, and europium in solution.

Lanthanum is comparatively easily separated from the others, owing to the fact that its hydroxide has a more strongly basic character and is more soluble in the presence of ammonium chloride.[1] By slowly adding to a warm solution of the mixed chlorides (containing ammonium chloride) small quantities of ammonia (also containing ammonium chloride), the solution being stirred during the addition, practically all the less basic and less soluble hydroxides are separated in the first portions, and comparatively pure lanthanum chloride is left in solution; the lanthanum can then be thrown down as hydroxide by adding a further quantity of ammonia. The various fractions of the precipitate are redissolved in acid, and the fractional precipitation process is repeated, until sufficiently complete separation has been arrived at.

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[1] W. Prandtl and J. Rauchenberger, *Ber.* **53** (1920), 843; *Zeitsch. Anorg. Chem.* **120** (1921), 120.

Alternatively the whole of the metals present can be precipitated as the hydroxides, which are then treated with small quantities of bromine water; the lanthanum dissolves most freely in the first portions, and by repeating the process two or three times, pure preparations of lanthanum, free from the other metals, are obtained.[1]

Of the less basic metals members of the cerium family praseodymium, neodymium, samarium, europium and gadolinium, the first two are always present in the largest quantities. The separation of the five metals is accomplished by repeated fractional crystallization as :—

(*a*) double ammonium nitrates of type
$M(NO_3)_3.2NH_4NO_3.4H_2O$;

(*b*) double manganese nitrates of type
$2M(NO_3)_3.3Mn(NO_3)_2.24H_2O$; or

(*c*) double magnesium nitrates of type
$2M(NO_3)_3.3Mg(NO_3)_2.24H_2O$.

The order of solubility is the order of atomic weight, the praseodymium salts being the least soluble, and the gadolinium salts the most soluble. Thus praseodymium tends to collect in the early crystallizing fractions, neodymium in the middle fractions, whilst the three rarer elements tend to remain in the mother liquor. Where **praseodymium** and **neodymium** are to be prepared the ammonium or manganese methods are preferable. But if an attempt is to be made to obtain pure compounds of **samarium**,[2] **europium**,[3] or **gadolinium**,[4] the double magnesium salts are more satisfactory. The separation of the two last named elements is particularly difficult. It happens, however, that bismuth magnesium nitrate has practically the same solubility as the europium compound. By adding a moderate quantity of bismuth nitrate to the solution, most of the europium crystallizes out along with the bismuth, and can thus be separated with it. The subsequent removal of bismuth from europium by means of hydrogen sulphide is comparatively easy. Gadolinium is best purified by fractional crystallization as the dimethylphosphate.

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[1] P. E. Browning, *Comptes Rend.* 158 (1914), 1679.

[2] O. J. Stewart and C. James, *J. Amer. Chem. Soc.* 39 (1917), 2605; A. W. Owens, C. W. Balke and H. C. Kremers, *J. Amer. Chem. Soc.* 42 (1920), 515.

[3] G. Urbain and H. Lacombe, *Comptes Rend.* 138 (1904), 627; C. James and J. E. Robinson, *J. Amer. Chem. Soc.* 33 (1911), 1363.

[4] L. Jordan and B. S. Hopkins, *J. Amer. Chem. Soc.* 39 (1917), 2614.

By patient fractionation all the members of the cerium family have been prepared in a state of moderate purity.

Separation of the Metals of the Yttrium Family

The yttrium family occur together in nature in such minerals as gadolinite and euxenite, but the separation of the different members in a pure state is a most tedious operation.

Yttrium is by far the most abundant element of the family, and is probably most conveniently separated from the other metals by fractional precipitation of the metals as chromates, through the addition of potassium chromate to a solution of the oxides in chromic acid.[1] The chromates of the heavier metals are most insoluble, and yttrium tends to accumulate in the filtrate, but the method must be repeated a large number of times before pure yttrium salts can be obtained. For the removal of the last traces of erbium and holmium, fractional precipitation with sodium nitrite is said to be the most efficient method.[2]

Many alternative separation methods are known for concentrating the other earths of the yttrium group. All are lengthy and troublesome. By repeated fractional crystallization of the **formates**,[3] three principal portions are obtained. Of these, the lightest and most soluble portions can be worked up to give pure yttrium salts, whilst from less soluble portions other members of the family have been isolated.

A more general method of separating the individuals of the yttrium family is by fractional crystallization as **bromates.**[4] The rare-earth sulphates can be converted to bromates by double decomposition with barium bromate. The order of the solubility of the bromates is given below; it is roughly the order of atomic numbers, except that yttrium and scandium (which have much lower atomic numbers than the others) are out of place :—

(*Least soluble*) Tb, Dy, Ho, Y, Er, Tu, Yt + Lu, Sc (*most soluble*).

The fractionation of the bromates is continued until about twenty fractions are obtained. These can be classified as :—

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[1] J. E. Egan and C. W. Balke, *J. Amer. Chem. Soc.* **35** (1913), 365; H. C. Holden and C. James, *J. Amer. Chem. Soc.* **36** (1914), 642.

[2] B. S. Hopkins and C. W. Balke, *J. Amer. Chem. Soc.* **38** (1916), 2332.

[3] A. Bettendorff, *Lieb. Ann.* **352** (1907), 88.

[4] C. James, *J. Amer. Chem. Soc.* **30** (1908), 182, 979.

(1) Least soluble fractions; almost colourless yttrium bromate, containing traces of terbium, and usually small amounts of Sm, Eu, Gd, belonging to the cerium family.

(2) Yellowish fractions consisting of impure yttrium bromate, which shows the absorption bands of dysprosium and holmium.

(3) Pinkish fractions, consisting of yttrium bromate containing erbium.

(4) Fractions of yttrium bromate containing thulium, but still coloured pink with erbium.

(5) Most soluble fractions. Mother liquors containing ytterbium with lutecium, scandium, and also some thulium.

From the different fractions, the different elements can be prepared in special ways. The least soluble portions of the bromates can be recrystallized again, and, with patience, fairly pure bromate of **terbium** is obtained.[1] It is, of course, necessary to start with a very large amount of raw material, if any appreciable quantity of terbium salt is to be prepared.

The separation of **dysprosium**[2] from the kindred elements is best finished by means of the fractional crystallization of the "ethylsulphate" from alcoholic solution and at a fairly low range of temperatures (9–40° C.). The process is very laborious. About sixty recrystallizations may be needed in this final stage of the process alone, and the product will still contain traces either of holmium or terbium.

The isolation of **holmium** salts[3] is especially difficult on account of the minute quantities in which the element occurs, and on account of its close relationship with yttrium, which is generally present in comparatively large quantities. The fact that yttrium salts are colourless and show no absorption bands in spectroscopic examination makes the separation particularly difficult to follow. Fractional precipitation with sodium nitrite is said to give fair results whilst fractional crystallization as nitrate, and fractional precipitation with ammonia have been employed.

Erbium[4] is present in considerably larger quantities than holmium, and has been obtained in the form of quite pure salts. The separation from yttrium, which is naturally the main impurity can be brought about by fractional precipitation with sodium nitrite

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[1] C. James and D. W. Bissel, *J. Amer. Chem. Soc.* **36** (1914), 2060.

[2] G. Urbain, *Comptes Rend.* **142** (1906), 785; H. C. Kremers, B. S. Hopkin and E. W. Engle, *J. Amer. Chem. Soc.* **40** (1918), 598.

[3] L. F. Yntema and B. S. Hopkins, *J. Amer. Chem. Soc.* **40** (1918), 1163 O. Holmberg, *Zeitsch. Anorg. Chem.* **71** (1911), 226; H. C. Kremers and C. W. Balke, *J. Amer. Chem. Soc.* **40** (1918), 593.

[4] E. Wichers, B. S. Hopkins and C. W. Balke, *J. Amer. Chem. Soc.* **40** (1918) 1615.

An older method which gives good results is to fuse the mixed nitrates of yttrium and erbium, so as to cause partial decomposition. It is found that erbium nitrate decomposes more easily than yttrium nitrate. If, therefore, the partly decomposed mass is extracted with water, and the liquid obtained is filtered, so as to separate the soluble nitrate from the insoluble basic nitrate or oxide produced by the decomposition, the yttrium will tend to become concentrated in the filtrate, and the erbium in the insoluble residue; the residue is reconverted to nitrate, and the process is repeated.[1]

Thulium[2] can be separated in a fairly pure state by oft-repeated recrystallization as bromate. Being present in minerals in only very minute quantities, it is necessary to start with a very large amount of raw material.

Ytterbium, lutecium and scandium occur in the most soluble fractions obtained by the bromate method. **Scandium**, although generally regarded as a member of the yttrium family, has a double sulphate much less soluble than ytterbium, and by saturating the neutral solutions with potassium sulphate, the double sulphate of scandium and potassium is precipitated.[3] The filtrate contains ytterbium and lutecium, and can be precipitated by oxalic acid to give the oxalates, which are then ignited to give the mixed oxides.

The mixture of oxides of ytterbium and lutecium thus obtained was regarded until about 1905 as a pure substance, being called *ytterbia*. But between 1905 and 1907 Urbain[4] carried out a long research which enabled him to show that it consisted of two components. To the major component he gave the name "**neo-ytterbium**" to distinguish it from the mixture previously styled ytterbium, whilst the newly separated minor constituent he called **lutecium**. Urbain's method of separation consisted in crystallizing the mixed nitrates from a solution containing free nitric acid, the progress of the operation being followed by measuring the magnetic properties of the various fractions. About two hundred series of recrystallizations (involving 4,000 separate crystallizations in all) were needed before pure neo-ytterbium could be isolated, the work occupying about two years. Lutecium has not been prepared pure.

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[1] A modification of this process is described by P. H. M. P. Brinton and C. James, *J. Amer. Chem. Soc.* **43** (1921), 1397.

[2] C. James, *J. Amer. Chem. Soc.* **33** (1911), 1332.

[3] C. James, *J. Amer. Chem. Soc.* **30** (1908), 991. Other methods of obtaining scandium are described by E. J. Meyer, *Zeitsch. Anorg. Chem.* **86** (1914), 257; R. and G. Urbain, *Comptes Rend.* **174** (1922), 1310.

[4] G. Urbain, *Comptes Rend.* **145** (1907), 759; J. Blumenfeld and G. Urbain, *Comptes Rend.* **159** (1914), 323.

The two "Missing Elements." It is natural to ask whether any of the recent researches on the rare earths have pointed to the existence of the two undiscovered rare-earth metals. Several "new elements" have indeed been described from time to time, but, in most cases, they were probably really mixtures.[1] It is doubtful whether any well-supported claim has been made—up to the time of writing—to the discovery of the missing element between neodymium and samarium. But recent researches seem to indicate that the element of atomic number 72 exists in quite important quantities (up to 10 per cent.) in certain zirconium minerals found in Norway,[2] and elsewhere. A study of the X-ray spectrum indicates that the atomic number of the new metal is actually 72. The new element has been named *Hafnium*. The chemical properties of hafnium—so far as they are known—seem to be extremely similar to those of zirconium, the element with which hafnium is associated in nature; it seems, therefore, that hafnium must properly be regarded as a member of Group IVA rather than as a rare-earth element. If so, we can say that the "orderly sequence" of the elements in the periodic table commences, not at tantalum (Group VA) but at the preceding element, hafnium (Group IVA); it is interesting to note that this is quite consistent with the Bohr theory of the atom.

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[1] See for instance C. A. von Welsbach, *Zeitsch. Anorg. Chem.* **71** (1911), 439; *Monatsh.* **34** (1913), 1713; *Lieb. Ann.* **351** (1907), 458; compare G. Urbain, *Zeitsch. Anorg. Chem.* **68** (1910), 236; J. Blumenfeld and G. Urbain, *Comptes Rend.* **159** (1914), 323.

[2] D. Coster and G. Hevesy, *Nature* **111** (1923) 79, 182. Compare A. Scott, *Trans. Chem. Soc.*, **123** (1923), 311., G. Urbain and A. Dauvillier, *Nature*, **111** (1923), 218.

ACTINIUM

Atomic weight 226

Actinium, the last member of Group IIIA, has been mentioned in the chapter on radioactivity. It is probably a product of decay of uranium, the immediate parent being the unisolated element eka-tantalum. Although we know that actinium must give off β-rays when it gives rise to radio-actinium, yet the radioactivity is so feeble that it is often described as being rayless. The activity of the so-called "actinium preparations" is almost entirely due to the descendants of actinium.

Chemically speaking, actinium has little interest. It resembles lanthanum so closely that it would certainly be described as a "rare-earth element," if it happened to occur mainly in the same minerals as the other rare earths. The salts are colourless, and resemble those of lanthanum in their appearance and solubility relations. The hydroxide is gelatinous, and slightly more strongly basic than that of lanthanum.

Actinium occurs in pitchblende and other uranium ores, having been formed, probably, through the radioactive transformation of what were originally uranium atoms. From the acid solution of pitchblende, the radium (with lead and barium) may be precipitated as sulphate, and then the polonium (with bismuth, etc.) as sulphide; finally the actinium (with iron, lanthanum, etc.) is precipitated with ammonia. If the mixed hydroxides are worked up as though for the separation of lanthanum, the actinium is separated with the lanthanum. Finally, when a fairly pure lanthanum-actinium preparation has been obtained, the two metals are converted to the state of double magnesium nitrates, by the fractional crystallization of which a partial separation of lanthanum and actinium is possible.

When first separated, salts of actinium are scarcely radioactive, but the activity increases steadily as the preparation is stored owing to the formation of the products of decay. After some months a preparation of actinium has very remarkable "emanating" power, giving off the radioactive gas "actinium emanation." If an old actinium preparation is held up near to a zinc sulphide screen, the screen becomes luminous whenever the slight currents existing in the air happen to blow the emanation on to the surface of the screen.

GROUP IV$_A$

	Atomic Weight.
Titanium	48·1
Zirconium	90·6
Cerium	140·25
Thorium	232·15

The elements of Group IV$_A$ usually exert a valency of four, forming stable oxides of the type MO_2, although two members of the group, titanium and cerium, also form lower compounds, in which the element is trivalent. As in the case of boron, the oxides have an acidic, rather than a basic, character; titanium has much in common with silicon, and is often regarded as a non-metal. The basic character of the oxide increases in the group with the atomic weight.

The infusible character of the oxides, met with in the last group, is found again in Group IV$_A$, and the tendency to form colloidal solutions and gelatinous precipitates also recurs. The elements possess fluorides of type MF_4 which combine with fluorides of potassium (or sodium) to form well-developed complex fluorides of the type $2KF.MF_4$, or $K_2[MF_6]$. The occurrence of the common *co-ordination number*, six, in the complex, is worth pointing out; it will be met with frequently in some of the later groups.

The new element hafnium, referred to on page 237, appears to be properly a member of group IV$_A$.

TITANIUM

Atomic weight 48·1

Titanium is frequently classed with the non-metals and will only be discussed briefly in this volume. The more important oxide, TiO_2, is distinctly acidic in character, and forms titanates resembling closely the silicates. Nevertheless basic properties are not wholly lacking, for sulphates derived from both oxides have been obtained in the solid state.

The Element

The element is not often met with in a state of purity. As usually prepared, it is a shining grey powder, or a steel-like mass, very hard and brittle. Pure titanium, however, is fairly malleable, especially when hot. It melts at 1,795° C. Titanium combines readily with oxygen, nitrogen and carbon at high temperatures. When burnt in air, a mixture of oxide and nitride is formed. The equilibrium value of the electrode potential of titanium is unknown, but, since titanium dissolves in dilute acids with evolution of hydrogen, it clearly falls on the " reactive side " of hydrogen in the Potential Series.

Laboratory Preparation. The difficulties connected with the preparation of elemental titanium are due to its great affinity for oxygen and other non-metals. When the dioxide (TiO_2) is heated with sodium, for instance, the product still contains oxygen ; when reduction with carbon is attempted, the product usually contains carbon. Often when oxygen and carbon have been eliminated, the material produced is found to have taken up nitrogen, and for a long time titanium nitride was actually regarded as metallic titanium. However, by heating titanium chloride in a special form of bomb with sodium, beads of fairly pure titanium have been obtained.[1] By the careful use of a hammer, these beads can be forged into small rods at a red heat. Another method of preparing titanium consists in passing a mixture of titanium chloride vapour and hydrogen over sodium hydride, heated at 400° C. By this method a grey crystalline powder, consisting of pure titanium, can be obtained.[2]

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[1] M. A. Hunter, *12th Int. Cong. App. Chem.* (1912), Sect. II, 125 ; D. Lely and L. Hamburger, *Zeitsch. Anorg. Chem.* **87** (1914), 228.

[2] M. Billy, *Comptes Rend.* **158** (1914), 578.

Compounds

The main compounds are derived from the two oxides, Ti_2O_3 and TiO_2. The former is basic, but the salts are unstable, and act as powerful reducing agents. The latter is both acidic and basic; it forms titanates with alkalis, but, on the other hand, forms easily hydrolysable salts with acids.

A. Compounds of Tetravalent Titanium (Titanic Compounds [1]).

Titanic oxide, TiO_2, is formed when the element or the lower oxide is heated in oxygen, and is a white infusible substance. In a hydrated form it is produced by precipitation from a titanate or titanic salt. The variety produced when a cold solution of titanic chloride is treated with alkali is a voluminous white precipitate containing much water, and sometimes regarded as *orthotitanic acid,* $Ti(OH)_4$ or H_4TiO_4. When obtained by the hydrolysis of a boiling titanic chloride solution, a denser form containing less water is obtained, frequently regarded as *metatitanic acid,* $TiO(OH)_2$ or H_2TiO_3. Whether or not these are definite compounds is still very uncertain. As often happens, the voluminous form (" orthotitanic acid ") is readily soluble in dilute acids, whilst the denser form (" metatitanic acid "), which is produced at a higher temperature, is only very slowly dissolved. It is quite possible that the difference between the products obtained at different temperatures lies merely in their state of aggregation (as in the case of beryllium hydroxide), the primary particles being bigger in the precipitate obtained from a hot solution. Anhydrous titanic oxide is almost unattacked by acids, no doubt on account of its compact character.

Titanic acid is readily obtained as a colloidal solution. The solution of titanic chloride obtained by dissolving titanic acid in hydrochloric acid is considerably hydrolysed, and if the majority of the hydrochloric acid is gradually removed by dialysis, a colloidal solution of titanic acid is left. If the liquid produced contains more than about 1 per cent. of titanic acid, it is apt to gelatinize spontaneously.[2]

By treating potassium titanate with a small quantity of concentrated acid, at ordinary temperatures, a clear liquid is obtained which gradually becomes opaque and gelatinous. The gelatinous mass, which consists essentially of titanic acid, can be washed on a filter.[1] On boiling with water, it gives the ordinary form of metatitanic acid.

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[1] Some authorities, including Abegg, use the term " titanic " for the compounds of trivalent titanium, reserving the word " titanous " for the unstable compounds of divalent titanium.

[2] T. Graham, *Comptes Rend.* **59** (1864), 181.

Titanates. The titanates are formed when titanic acid is dissolved in a solution of an alkali, or when the anhydrous oxide is treated with a fused alkali. **Potassium titanate,** K_2TiO_3, obtained by the method of fusion, is described as a yellow, fibrous mass. A hydrate, $K_2TiO_3.4H_2O$, can be obtained by crystallization from a solution of titanic acid in caustic potash. The titanates of **calcium** ($CaTiO_3$) and of **iron** ($FeTiO_3$) are insoluble, and occur in nature.

Titanic Salts. As has been mentioned, the so-called "orthotitanic acid" is soluble in dilute acids. The solutions, which are colourless, are strongly hydrolysed, and in general the solid normal salt cannot be obtained by evaporation. Thus a solution in sulphuric acid yields only a **basic sulphate** on boiling. The **normal sulphate,** $Ti(SO_4)_2.3H_2O$, is, however, obtained by the oxidizing action of concentrated nitric acid upon titanous sulphate; prepared in this way it is stated to have a yellowish colour. Similarly, the solution of titanic oxide in hydrochloric acid contains to a small extent the **chloride,** $TiCl_4$; but, since complete hydrolysis occurs when the solution is evaporated, the chloride must be isolated in a different way. It is obtained when chlorine is led over a heated mixture of titanic oxide and carbon, and is found to be a volatile odorous liquid, boiling at 136° C., resembling the tetrachlorides of silicon, tin and germanium. The **fluoride** (TiF_4) is formed in solution when "orthotitanic acid" is dissolved in excess of hydrofluoric acid. It is difficult to isolate the simple fluoride from this solution, but when potassium fluoride is added, the complex salt **potassium titanifluoride,** K_2TiF_6, which has a rather low solubility (0·6 per cent. at 0° C.), separates out in thin colourless monoclinic crystals. This salt is analogous to the silicofluorides and germinifluorides, and appears to ionize as a complex salt $K_2[TiF_6]$. Numerous other titanifluorides are known.

B. Compounds of Trivalent Titanium (Titanous Compounds).

Titanous oxide, Ti_2O_3, is obtained in the anhydrous condition when titanic oxide is heated in hydrogen; it is black or reddish-brown, according to the conditions of formation. The corresponding hydroxide, $Ti(OH)_3$, is thrown down as a brown precipitate by the action of ammonia on a titanous salt solution.

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[1] A. F. von der Pfordten, *Lieb. Ann.* 237 (1887), 213.

Titanous Salts are formed in solution when the titanic salts are reduced by means of metallic zinc or by electrolysis, or when titanium dissolves in dilute acids with the exclusion of air. The solutions possess a violet colour and have strong reducing properties, converting ferric to ferrous compounds ; a trace of titanous salt solution added to gold chloride causes a most intense coloration, probably due to colloidal gold; this colour is visible at a dilution of 1 in 20,000,000. Titanous salt solutions are oxidized readily by atmospheric oxygen, colourless titanic compounds being formed.

Several solid titanous salts have been isolated by the crystallization of the solutions. The **sulphate**, $Ti_2(SO_4)_3.3H_2O$, forms blue crystals. The **chloride**, $TiCl_3.6H_2O$, which has been obtained by concentration of the solution *in vacuo*, possesses a violet colour. The anhydrous chloride is formed by the action of hydrogen on the tetrachloride. The reaction,

$$2TiCl_4 + H_2 = 2TiCl_3 + 2HCl$$

is nearly complete at 1,200° C., but at lower temperatures, an equilibrium is set up between the tetrachloride and trichloride ; the continuous formation of the latter at these lower temperatures is only possible if it is removed from the vaporous phase as fast as it is formed. For instance, if a mixture of titanium tetrachloride vapour and hydrogen is passed through the annular space between two co-axial quartz tubes, the inner one being heated electrically to about 1,100° C, whilst the outer one is cooled externally with water, a red-violet powder, consisting of the trichloride ($TiCl_3$) collects on the inside of the outer tube.[1]

The presence of colour in the titanous compounds is worthy of notice. We always seem to obtain coloured compounds when a metal departs from its normal valency.

C. Other Compounds of Titanium.

A lower oxide, TiO, is said to be formed when titanic oxide is heated with magnesium to redness ; a black powder is obtained, but it may be a mixture, or perhaps a solid solution of oxygen in titanium. It is stated that a hydrated form of the same oxide is obtained as a black precipitate when an acidified solution of potassium titanifluoride is reduced with sodium amalgam. The corresponding **chloride**, $TiCl_2$, is obtained as a black or brown powder when titanous chloride is heated at 660–700° C. in a current of hydrogen,

$$2TiCl_3 \rightleftharpoons TiCl_4 + TiCl_2$$

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[1] H. Goerges and A. Stähler, *Ber.* **42** (1909), 3200 ; A. Stähler and F. Bachran, *Ber.* **44** (1911), 2906.

The volatile tetrachloride passes away, whilst the dichloride remains behind. Titanium dichloride takes fire when exposed to air; it dissolves in water, giving a solution which is at first colourless, but which quickly decomposes, hydrogen being evolved, and violet titanous chloride being produced.

Titanium Peroxide. When hydrogen peroxide is added to a titanic salt, a yellow colour appears, due to a higher oxide or a salt of such an oxide. If the solution contains alcohol, and is afterwards treated with ammonia, a yellow precipitate of the hydrated peroxide slowly separates.[1] The peroxide is usually stated to have the composition $TiO_3.nH_2O$, but recent investigations[2] appear to suggest the formula $Ti_2O_5.nH_2O$.

Nitrides.[3] Two nitrides of titanium are known to exist. They can be formed directly by the action of nitrogen on the metal. At very high temperatures, nitrogen will turn out oxygen from combination with titanium, and nitrides have actually been prepared by heating the oxide in nitrogen in the electric furnace. The nitrides of titanium possess a metallic lustre, and were long mistaken for metallic titanium.

Titanic nitride, Ti_3N_4, is formed by the action of ammonia on titanic chloride; when, for instance, vapours of titanic chloride and ammonium chloride are passed through a red-hot tube, the nitride is obtained as a copper-red crust of small crystals. **Titanous nitride,** TiN, is formed when titanic nitride is heated in a current of hydrogen, but is more readily prepared by the action of ammonia upon heated titanous oxide, or even upon titanic acid; in the latter case, the reaction is very slow because the titanic oxide must first be reduced to titanous oxide by the hydrogen arising from the decomposition of ammonia. Titanous nitride is a brass-yellow substance; the fine powder, when suspended in water, appears yellow by reflected light, and blue by transmitted light.

Analytical

When an acidified solution containing a titanium compound is treated with metallic zinc, a violet coloration (due to a titanous salt) is produced. This test is not very delicate, as the violet colour is far from intense; probably the extremely intense coloration obtained by adding gold chloride to a titanous salt, recommended primarily as a test for gold,[4] would serve also as a test for titanium;

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[1] L. Lévy, *Comptes Rend.* 108 (1889), 294.

[2] M. Billy, *Comptes Rend.* 172 (1921), 1411.

[3] C. Friedel and J. Guérin, *Comptes Rend.* 82 (1876), 972.

[4] A. Stähler and F. Bachran, *Ber.* 44 (1911), 2914.

but it must be remembered firstly that titanous solutions oxidize very rapidly through contact with air, and secondly that certain other substances, notably stannous salts, produce a coloration with gold chloride.

The fine yellow coloration produced by the addition of hydrogen peroxide has also been used for the detection of titanium; the test is not reliable in the presence of much hydrofluoric acid.

Solutions of titanic salts are precipitated by ammonia, along with iron and aluminium. Even without the addition of alkali, however, titanic salt solutions containing acetic and sulphuric acids hydrolyse when boiled, titanic acid being precipitated. A method of separation from iron depends on this hydrolytic reaction; prolonged boiling (8–10 hours) is needed in order that the precipitation of the titanium shall be complete.[1] A rather similar method, in which the titanium is precipitated by boiling a solution containing acetic acid and sodium acetate, has been applied to the separation of titanium from aluminium; but the precipitation must be repeated three times before the separation is complete.[2] The separation from zirconium is discussed in connection with that element.

Minerals containing titanium are often very difficult to decompose, being usually unaffected by acids. It is customary to grind them very finely and fuse with potassium bisulphate; afterwards the fused mass can be extracted with water.

Clearly, in many of the analyses of minerals published in the past, the titanium oxide has been left along with the silica in the insoluble residue, and the weight of silica shown in the statement of the analysis includes titanium oxide.

TERRESTRIAL OCCURRENCE

Titanium is actually one of the most common elements that help to compose the earth's crust; but although it is very widely distributed throughout rocks, titanium minerals are in most cases only minor constituents of the rock-mass. In practically all types of igneous rock titanium compounds are met with. In basic rocks, which are usually rich in iron, it crystallizes out as the iron titanate, known as

Ilmenite . . $FeTiO_3$.

Great masses composed mainly of ilmenite occur in Scandinavia and elsewhere; the well-known "titaniferous iron ores" consist partly of ilmenite, but partly of magnetite (Fe_3O_4) containing titanium as an impurity. In rocks of a less basic character, titanium usually crystallizes out as the calcium compound known as

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[1] G. Streit and B. Franz, *J. Prakt. Chem.* 108 (1869), 65. See also *Zeitsch. Anal. Chem.* 9 (1870), 388.

[2] F. A. Gooch, *Chem. News*, 52 (1885), 68.

Sphene (titanite) . . $CaO.TiO_2.SiO_2$.

Where the magma has been deficient both in calcium and iron—as in many acid rocks—free titanic oxide may be produced. This occurs in three crystalline forms

Rutile (tetragonal) }
Brookite (rhombic) } . . . TiO_2
Anatase (tetragonal) }

Rutile is the form commonly found in fresh granites, but the other two are formed by secondary changes and are not uncommon in altered rocks.

The titanium minerals evidently crystallize much more readily than the silicates and other constituents of the magma. The crystals have apparently developed whilst the magma in which they were suspended was still liquid, and—in contrast to many of the silicate minerals—their crystalline form has not been interfered with by contact with other crystals growing on each side of them. Sphene, in particular, forms well-developed crystals, which are well-known to petrologists as constituents of syenites and granites; they may be seen in the rock-sections as light-brown pleochroic acute-angled crystals. Rutile occurs in granites in needle-shaped crystals which are seen piercing quartz and felspar, having actually been formed, of course, long before the quartz and felspar in question. In addition, smaller quantities of titanium occur in many minerals of which the element is not an essential component. Apparently titanium atoms can replace atoms of tetravalent silicon in the crystal structure; but in other cases we find titanium replacing trivalent elements like iron. Some micas contain titanium, whilst many iron minerals, besides ilmenite, contain appreciable quantities of the element; magnetite, for instance, is often titaniferous.

The sedimentary rocks derived from igneous rocks also contain titanium; many clays, shales and slates contain minute needles, commonly known as "clay-slate needles," which are actually crystals of rutile.

TECHNOLOGY AND USES

The presence of titanium in minerals is often of considerable economic importance, although, in some cases, instead of adding to their value, it detracts from it. Iron ores containing titanium, for instance, present difficulty in smelting, since an infusible substance containing titanium forms in the blast-furnace and tends to interfere with the descent of the charge. Although the trouble can be overcome by suitable modification of the process, titaniferous ores are—in ordinary practice—avoided.

There are, however, many purposes for which titanium is actually useful. Owing to its high affinity for oxygen and nitrogen, it is suitable for adding to steel as a "cleanser" just before the steel is cast into ingots; it combines with the non-metals, which would otherwise cause intergranular weakness and general unsoundness. The titanium is actually added as **ferro-titanium,** an alloy of iron and titanium, or **ferro-carbo-titanium,** which is cast iron containing both graphite and titanium carbide. These alloys are made by smelting titaniferous iron ores with coal or coke in the electric furnace, scrap iron being often added to the charge.[1] The process is further referred to in the section on ferro-alloys (Vol. III).

During the war, owing to the shortage of manganese, the use of titanium as a deoxidizer in steel became quite common.[2] Especially was this the case in America, where rails made of steel treated with titanium appear to have given excellent results.

Titanium oxide (rutile) has found considerable application in the preparation of enamels for coating iron vessels.[3] Its *rôle* is essentially that of an opacifier, the refractive index being very much higher than that of the body of the enamel. In addition, enamels containing titanium are said to be more durable, and to protect the iron better from corrosion than ordinary enamels. Titanium enamels are largely used in the manufacture of artificial teeth.[4]

The employment of titanium oxide as a constituent of pigments also depends on the high refractive index; one white pigment now manufactured in Norway and the United States consists of barium sulphate and titanic oxide.[5]

The main source of the rutile required for industrial purposes appears to be basic igneous rocks. Certain rocks, occurring in Virginia, contain both ilmenite and rutile in commercially important quantities; the minerals are separated from one another by magnetic means.[6]

The liquid anhydrous chloride was used to some extent in the late war for the production of smoke clouds. The vapour reacts in damp air to produce fine particles of a hydrate $TiCl_4.5H_2O$. If ammonia vapour is mixed with the titanium chloride, a better cloud is obtained, an additive compound being formed. Silicon chloride was also largely used for the same purpose; but, possibly owing to the higher refractive index of titanium compounds, a better obscuring power is normally obtained with titanium.[1]

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[1] G. F. Comstock, *J. Soc. Chem. Ind.* **34** (1915), 55; B. Stoughton, *J. Franklin Inst.* **177** (1914), 65.

[2] W. A. Janssen, *Iron Age*, **98** (1916), 31. See also experiments on the magnetic properties of iron deoxidized by titanium, described by M. A. Hunter and J. W. Bacon, *Trans. Amer. Electrochem. Soc.* **37** (1920), 513.

[3] *J. Soc. Chem. Ind.* **39** (1920), 271R; R. R. D. Landrum and L. J. Frost, *J. Amer. Ceram. Soc.* **3** (1920), 316.

[4] E. Cahen, *Discovery*, **1** (1920), 141.

[5] *J. Soc. Chem. Ind.* **41** (1922), 209R, 216R.

[6] *Eng. Min. J.* **95** (1913), 226.

Titanium compounds, notably the carbide, are sometimes used in the electrodes of electric arc lamps; others have also found application, as mordants, in dyeing.[2]

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[1] G. A. Richter, *Trans. Amer. Electrochem. Soc.* **35** (1919), 323.
[2] F. L. Hess, *U.S. Geol. Surv., Min. Res.* (1918), 810.

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ZIRCONIUM

Atomic weight 90·6

The Metal

Zirconium generally resembles titanium, which falls above it in the periodic scheme, but also has many properties in common with germanium, which falls into Group IVB. The element has a steel-grey colour, and is very hard; when polished, it displays a bright metallic lustre. Like titanium, it has a very high melting-point.

The electrode potential of zirconium is uncertain, but it is probably an active element, the activity being often obscured, as in the case of aluminium, through the presence of a permanent oxide-film. In fact, the behaviour towards reagents in many ways recalls that of aluminium. It is only slowly attacked by acids, with the exception of hydrofluoric acid, which dissolves it quite quickly. Similarly the compact metal is quite resistant towards atmospheric corrosion, and is only very slightly oxidized even when strongly heated. But the finely divided element oxidizes much more readily, and may even "catch fire" if warmed in air.

It is interesting to note that a zirconium anode, like an aluminium anode, displays valve-action.[1]

Laboratory Preparation. The element can be obtained by the action of an alkali metal or of magnesium on one of the halogen salts, or by reduction of the oxide with carbon at a rather high temperature. In the latter case the product is liable to contain carbon if the latter is in excess, and will retain some oxygen if the carbon is not in excess. It is better therefore to obtain the element by heating the double salt, potassium zirconifluoride, with magnesium in an electric furnace. Aluminium and sodium have also been used as reducing agents. The method of heating zirconium chloride with sodium in a bomb is said to give an almost pure product.[2]

Compounds[3]

Zirconium is tetravalent in practically all its compounds, which are derived from the oxide ZrO_2. A lower series of salts analogous to the titanous series is not known.

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[1] L. H. Walter, *Electrician*, 71 (1913), 1057.

[2] D. Lely and L. Hamburger, *Zeitsch. Anorg. Chem.* 87 (1914), 223.

[3] Much useful information will be found collected in F. P. Venable's "Zirconium and its Compounds" (1922) (American Chemical Society's Monographs).

Zirconium oxide (*zirconia*), ZrO_2, is obtained when the finely divided element is burnt in oxygen. It is obtained in a hydrated form as a white voluminous hydroxide, when a soluble salt, e.g. potassium zirconifluoride, is treated with ammonia, or when a zirconate undergoes hydrolysis. The hydroxide when ignited yields the hard white anhydrous oxide. The oxide is practically infusible, the melting-point being higher than that of any other oxide. According to Ruff [1] it is 2,585° C., and according to Podszus,[2] 3,000° C. —a somewhat notable discrepancy. Zirconium oxide becomes incandescent when heated, giving out an intense white light.

The freshly precipitated hydroxide is soluble in acids, zirconium salts being formed, but the anhydrous oxide is almost undissolved by acids. As in the case of the hydroxides of beryllium, aluminium and titanium, it is observed that zirconium hydroxide, when precipitated from a hot solution, dissolves less quickly than the precipitate obtained from a cold solution, being much denser in the first case. Moist zirconium hydroxide absorbs carbon dioxide from the air.

Zirconates. Although the hydroxide is scarcely soluble in aqueous alkalis, it is capable of forming zirconates when heated with fused alkaline hydroxides or carbonates. Compounds said to have the formulæ Na_2ZrO_3 and Na_4ZrO_4 have been described, but, as they are immediately hydrolysed by water, with the precipitation of hydroxide, it is difficult to be sure that they represent definite chemical compounds.

Zirconium Salts. The salts are obtained when the hydroxide is dissolved in the appropriate acids. There is a certain tendency towards hydrolysis, and the normal salts can only be obtained in the solid state from solutions containing free acid. But in addition to the normal salts of the type, ZrX_4, there are basic salts (*zirconyl salts*) of the type $(ZrO)X_2$, which are often more stable. The "zirconyl" salts are undoubtedly chemical individuals, having been obtained in well-defined crystals of constant composition; but some of the other basic salts described by the earlier writers are probably adsorption products.[3]

Zirconium **sulphate** forms colourless crystals having the composition $Zr(SO_4)_2.4H_2O$; it loses three of the four molecules of water when heated at 120° C. Some chemists[1] consider that, properly speaking, it should be regarded as an acid zirconyl sulphate, $(ZrO)SO_4.H_2SO_4.3H_2O$, or as a zirconyl-sulphuric acid, $[(ZrO)(SO_4)_2]H_2.3H_2O$; such a view will explain why one of the four molecules of water is more firmly attached than the others. When the solution is heated for a long time above 40° C., hydrolysis occurs, an insoluble "basic salt" being precipitated.

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[1] O. Ruff, *Zeitsch. Anorg. Chem.* 82 (1913), 390.

[2] E. Podszus, *Zeitsch. Angew. Chem.* 30 (1917), 17.

[3] A. Müller, *Zeitsch. Anorg. Chem.* 52 (1907), 316, supports the adsorption view for all zirconium basic salts. A. Rosenheim and P. Frank, *Ber.* **40** (1907), 803, urge that the zirconyl salts are true individuals. A new type of basic salt is described by E. H. Rodd, *Trans. Chem. Soc.* **111** (1917), 396. Another view of the behaviour of zirconium salts in solution is given by M. Adolf and W. Pauli, *Koll. Zeitsch.* **29** (1921), 173.

A **nitrate,** $Zr(NO_3)_4$, has been described, but more recent investigations[2] have failed to confirm its existence, although various hydrates of zirconyl nitrate, $ZrO(NO_3)_2$, are known. The **chloride** can be obtained by crystallization from a solution of the hydroxide in hydrochloric acid; partial hydrolysis is very liable to occur, and the final stages of the evaporation should be conducted in a current of hydrogen chloride gas. It is prepared more easily in the anhydrous condition ($ZrCl_4$) by the well-known method of passing dry chlorine gas over a heated mixture of the oxide and carbon but even the product of this dry method is very likely to contain the zirconyl chloride $(ZrO)Cl_2$, also known as zirconium oxychloride. The oxy-chloride has been isolated in the hydrated condition containing eight molecules of water, by crystallization from a solution of zirconium hydroxide in hydrochloric acid. It is itself fairly soluble in water, but if the solution is boiled for a long time, hydrolysis occurs, gelatinous zirconium hydroxide being precipitated.

Fluorides. When zirconium hydroxide is dissolved in hydrofluoric acid, the fluoride, ZrF_4, is produced. If the solution is mixed with a solution of potassium fluoride, a complex salt **potassium zirconifluoride,** K_2ZrF_6, which is comparatively insoluble, crystallizes out. When, however, the potassium fluoride is in excess, the precipitate formed has the composition $K_2ZrF_6.KF$. The zirconifluorides, which are perfectly analogous to the complex fluorides formed by the other tetravalent elements (titanium, silicon, germanium and tin), appear to ionize as complex salts of the type $M_2[ZrF_6]$. The potassium salt has a solubility of 1·4 per cent. at 15° C.

An important salt of zirconium is the oxalate, which is obtained by precipitation; it differs from the oxalates of the rare earths by being soluble in excess of oxalic acid and in ammonium oxalate.

Peroxide. When hydrogen peroxide is added to a solution of zirconium sulphate, a white peroxide is produced in a hydrated condition, to which the formula, Zr_2O_5, has been assigned.

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[1] R. Ruer, *Zeitsch. Anorg. Chem.* 42 (1904), 87.

[2] E. Chauvenet and L. Nicolle, *Comptes Rend.* 166 (1918), 781, 821.

A lower oxide (ZrO) has been described, but recent work has shown it to be a mixture of the dioxide and metal.[1]

Analytical

Turmeric paper, after being moistened with a solution of a zirconium salt containing hydrochloric acid, turns red-brown on drying.

Zirconium salts treated with ammonia yield a gelatinous precipitate of the hydroxide. The same precipitate is obtained by the addition of caustic soda; unlike the white hydroxides of aluminium and beryllium, it is insoluble in excess of alkali. The solubility in acids depends on the temperature of precipitation; it dissolves with difficulty when produced from a hot solution.

The addition of oxalic acid to zirconium salts produces a white precipitate of the oxalate; unlike the oxalates of the rare-earth metals, it is soluble in ammonium oxalate, or even in excess of oxalic acid. Thorium oxalate is also dissolved by ammonium oxalate, but is reprecipitated when hydrochloric acid is added, whilst zirconium remains in solution.

Zirconium salts are precipitated by potassium sulphate, an insoluble double sulphate being produced. Zirconium differs from titanium in that the salt solutions do not deposit insoluble basic salts when boiled in the presence of acetic acid.

The reactions given above can be utilized as the basis for the separation of zirconium from other metals, but the actual working processes are laborious, because many of the separations are incomplete, and the operations must be repeated if quantitative results are required.[2] A more convenient method of separating zirconium from aluminium and the rare-earth metals is by the addition of selenious acid to a solution containing hydrochloric acid. Zirconium is thrown down as a basic selenite, whilst aluminium and the rare earths remain in solution.[3] The basic selenite should be washed with 3 per cent. hydrochloric acid and dried; it yields the oxide, ZrO_2, on ignition.

The same method may be used to separate zirconium from a small amount of iron (in the ferric condition); but if much iron is present in the solution, the precipitate will contain iron, and the process must be repeated. If titanium is present, it will be precipitated with zirconium under ordinary circumstances; but if excess of hydrogen peroxide be added before precipitation, the titanium will remain in solution, and a separation is thus rendered possible.

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[1] R. Schwartz and H. Deisler, *Ber.* **52** (1919), 1896.

[2] For details of estimation in ores see G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.* **42** (1920), 1439.

[3] M. M. Smith and C. James, *J. Amer. Chem. Soc.* **42** (1920), 1764.

TERRESTRIAL OCCURRENCE

The geo-chemistry of zirconium is in some respects similar to that of titanium, the element occurring in small quantities distributed throughout large masses of rock. It is, however, less abundant than titanium, and is commoner in the acidic rocks than the basic. It is most frequently found as the silicate,

Zircon . . . . . . $ZrSiO_4$,

which is one of the commonest accessory minerals of granite and syenite. Like the titanium minerals, zircon is one of the earliest members of the magma to crystallize; consequently it is usually found in well-formed crystals, which belong to the tetragonal system; they are often small, but sometimes attain a considerable size. Zircon is characterized by the square pyramid in which the crystals usually terminate, as well as by its hardness and adamantine lustre. It may be colourless, but is often brownish-yellow or grey.

Certain rocks contain the zirconium as the oxide,

Baddeleyite (Brazilite) . . ZrO_2,

although this is rarer than the silicate. Zirconium is also a non-essential constituent of other rock-forming minerals. Certain pyroxenes, for instance, related to augite, contain zirconium.

When igneous rocks containing zircon undergoes weathering, the zirconium mineral remains comparatively undissolved, and is either left behind in the residual deposits or is carried off by the water in suspension. Since, however, zircon is much heavier than the majority of the insoluble minerals occurring in rocks, it is dropped comparatively readily by the running water, along with the coarser sand-particles. Thus the forces of Nature bring about a considerable concentration of the zircon, and, in the same way, of brazilite. These alluvial deposits are naturally a convenient source of zirconium compounds. Important deposits occur in the Caldas region of Minas Geraes (Brazil) and also in Ceylon. It is noteworthy that important ores of thorium (which have a similar mode of origin) are also found in the two countries just mentioned; in fact the beach deposits known as "monazite sand," which are so largely worked for thorium, almost always contain zirconium minerals.

Zircon is by far the commonest zirconium mineral in the alluvial deposits, but the oxide is industrially more useful, and is consequently more sought after. In Brazil, there occur in certain alluvial deposits pebbles, $\frac{1}{2}$–3 inches in diameter, consisting of a material called "zirkite," which is really a mixture of brazilite with zircon and other silicates; the pebbles contain over 90 per cent. of ZrO_2, whilst other forms of zirkite found in the same district carry about 80 per cent.[1]

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[1] E. H. Rodd, *J. Soc. Chem. Ind.* **37** (1918), 213R.

TECHNOLOGY AND USES

The present and future value of zirconium rests mainly on the unusually refractory character of the oxide. Zirconia has a very high melting-point, and in the ignited form is remarkably inert towards acids, fused alkalis, and silicates. It is unattacked by oxygen and only reacts with carbon and nitrogen at very high temperatures.[1] It is already employed in the manufacture of muffles, crucibles and pyrometer tubes; zirconium crucibles can be employed at temperatures up to 2,200° C.[2] and have been used for the melting of platinum. The coefficient of expansion is very low, so that zirconia articles can undergo sudden changes of temperature without cracking.[3] Zirconia pencils are used in Bleriot motor headlights. If the price could be reduced, it would no doubt be employed largely for the lining of furnaces; owing to the low heat-conductivity of zirconia, its employment in furnaces would tend to reduce the loss of heat by radiation.

At present the main source of zirconia for refractory purposes is the Brazilian oxide ores (baddeleyite or zirkite); but, if the demand for zirconia grows, it will be necessary to consider the manufacture of zirconium oxide from the silicate, zircon, which occurs in the monazite sands of India and Brazil, and is thus a bye-product of the thorium industry.[4]

The crude zirkite softens at a much lower temperature than pure zirconia, but even this impure form constitutes quite a good refractory. Naturally the lower softening-point makes it easier to burn; zirkite can in fact be made into firebricks without the addition of another substance as binder; it is, however, better to add a little china-clay to serve as a binder. Starch has also been used in the mixture in Germany. Where a still more refractory material is required, the zirkite must be purified. Even washing with sulphuric acid removes much of the iron, the most deleterious impurity, but more elaborate treatment is required to remove the remainder of the iron, as well as the silica. Various methods are available, the zirkite being ground and brought into solution by treatment with fused sodium carbonate, fused sodium bisulphite, or even with sulphuric acid. Zirconium is subsequently precipitated as basic sulphate, or some other insoluble salt, which can be ignited to yield the oxide. Purification is brought about by dissolution of the oxide in excess of hydrofluoric acid, followed by the addition of potassium carbonate; potassium zirconifluoride, which is only slightly soluble at low temperatures, crystallizes on cooling, and can be further purified by recrystallization.[1] When pure it can be precipitated with alkali, and the precipitate ignited to give the oxide.

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[1] *Chem. Zeit.* 42 (1918), 579.

[2] O. Ruff, *Zeitsch. Anorg. Chem.* 86 (1914), 389.

[3] H. C. Meyer, *Met. Chem. Eng.* 12 (1914), 791; 13 (1915), 263.

[4] W. Rosenhain, *Trans. Faraday Soc.* 12 (1917), 181.

The manufacture of pure white zirconia was started in this country a few years ago.[2]

Owing to the very high melting-point of pure zirconia, the manufacture of zirconia-ware presents many difficulties. Numerous experiments have been made, mainly in Germany, which seem to indicate that the use of clay in admixture for pure zirconia articles is unsatisfactory, but that by mixing a small amount of aluminium oxide or magnesium oxide with the zirconia, good results can be obtained.[3] Other oxides like thoria and yttria were tried with success.

A good deal of trouble has been experienced with zirconia articles owing to the excessive shrinkage when exposed to high temperatures, which caused cracks to appear. This can best be avoided by ensuring that the original ignition of the zirconia has been carried out at a sufficiently high temperature. If the zirconia is actually fused in an electric furnace, and then ground and made into articles, the articles so obtained practically do not shrink at all.[4]

Zirconia has also been used in optical glass and as a constituent of acid-proof enamel.

During the war, steel containing zirconium is said to have been used largely by the Germans for armour-piercing shells and for bullet-proof shields; experiments with zirconium steel have been carried out in America with a view to use in automobile construction.[5] The element is added to the steel as a ferro-zirconium alloy, and one of its functions appears to be that of a deoxidizer; the use of titanium for the same purpose will be remembered. Nevertheless it seems that zirconium, if added in sufficient quantity, has a specific effect on steel. A nickel-zirconium steel has apparently properties rather similar to a chrome-nickel steel, but is said to be stronger.

Some of the clearer varieties of zircon, which often have a yellow or red colour, have a value as gem-stones, the name "hyacinth" being applied to them.

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[1] J. W. Marden and M. N. Rich, *J. Ind. Eng. Chem.* **12** (1920), 651.

[2] *J. Soc. Chem. Ind.* **37** (1918), 254R.

[3] L. Weiss, *Zeitsch. Anorg. Chem.* **65** (1910), 218; O. Ruff, *Zeitsch. Anorg. Chem.* **86** (1914), 389; O. Ruff and G. Lauschke, *Zeitsch. Anorg. Chem.* **97** (1916), 73. See also E. H. Rodd, *J. Soc. Chem. Ind.* **37** (1918), 214R.

[4] E. Podszus, *Zeitsch. Angew. Chem.* **30** (1917), 17.

[5] J. Garcon, *Bull. Soc. d'Enc.* **131** (1919), 148.

CERIUM

Atomic weight . . . . 140·25

Cerium has been repeatedly mentioned in the consideration of the rare-earth metals, firstly because it occurs along with them in nature, and secondly because the *cerous* compounds, in which the metal is trivalent, are extremely similar to the compounds of the rare-earth metals. Zirconium and thorium have no salts of this type. At the same time, the *ceric* salts, in which the metal is tetravalent, are very similar to the salts of zirconium and thorium, but have no counterpart among the compounds of the rare-earth metals. For this reason cerium is considered in detail at this point.

The Metal

Metallic cerium resembles the rare-earth metals, and differs from zirconium and thorium, by melting at a comparatively low temperature (623° C.). It is a steel-grey metal, rather soft, but nevertheless capable of taking a good polish; when moderately pure, it is both ductile and malleable.

Cerium appears to be a highly reactive element, falling between magnesium and zinc in the Potential Series. If an oxide-film is formed upon the metal, it does not seem to protect it entirely, for cerium decomposes cold water slowly, hydrogen being evolved. The evolution of hydrogen is much more rapid in dilute acids, which dissolve the metal yielding cerium salts. The metal, moreover, tarnishes rapidly in damp air, and burns when heated in air, like magnesium, but more easily. Finely divided cerium takes fire spontaneously. Pure cerium is not pyrophoric, but the hard alloys containing iron give off sparks readily when rubbed with a file.[1] The element has powerful reducing properties.

Laboratory Preparation. The metal can be obtained by the electrolysis of the fused chloride contained in an iron pot which serves as cathode[2]; additions of sodium chloride, potassium fluoride and barium fluoride can be made in order to lower the melting-point. The graphite anode should be heated before being put into the mixture; otherwise the salt will solidify on the cold surface.

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[1] E. Weiss, *Zeitsch. Elektrochem.* **14** (1908), 549.

[2] A. Hirsch, *Met. Chem. Eng.* **9** (1911), 540; M. de K. Thompson, *Met. Chem. Eng.* **17** (1917), 213.

A rather high E.M.F. (10–15 volts) is usually employed. Molten cerium collects at the bottom of the pot.

Cerium can be purified from the most usual impurities by boiling with mercury, which dissolves the cerium, whilst the impurities rise as a scum to the surface, and are skimmed off. The mercury can afterwards be removed by distillation of the amalgam *in vacuo*.

Compounds

A. Compounds of Trivalent Cerium (Cerous Compounds).

Cerous **oxide**, Ce_2O_3, is rather difficult to obtain in the anhydrous condition. The **hydroxide**, $Ce(OH)_3$, is obtained as a white precipitate when ammonia is added to a cerous salt solution. The precipitate darkens when exposed to the air, higher hydroxides being formed.

The **salts** are produced when the metal, or the hydroxide, is dissolved in the appropriate acids. They are mostly colourless, and resemble closely the salts of the rare earths. The double **potassium cerium sulphate**, $3K_2SO_4.Ce(SO_4)_3$, is, as was stated in the section on rare earths, practically insoluble in excess of potassium sulphate, and is obtained by precipitation. It should probably be written $K_3[Ce(SO_4)_3]$. It is interesting to note that the three divalent $(SO_4)''$ radicles are equivalent to six univalent radicles. The salt affords, therefore, yet another example of the recurrence of the common *co-ordination number*, six, which occurs in the complex fluorides, like $K_2[TiF_6]$ and $K_2[ZrF_6]$.

The **oxalate**, like the oxalates of the rare earths, is insoluble in acids and is thrown down by the addition of an oxalate to a weakly acid solution of a cerous salt.

The anhydrous **chloride** can be produced by evaporating the solution of cerous hydroxide in hydrochloric acid. The indirect methods often required for the preparation of anhydrous chlorides are not necessary in the case of cerium.

B. Compounds of Tetravalent Cerium (Cerium Compounds).

The ceric compounds are analogous to the salts of zirconium and thorium, and are derived from the oxide, CeO_2. This oxide has feeble basic properties, but the salts are very easily hydrolysed.

Ceric oxide, CeO_2, is formed as a yellow or white powder when cerous nitrate is heated in the air. It is obtained in a hydrated condition when precipitated cerous hydroxide is oxidized with sodium hypochlorite solution. The hydrated oxide is lemon-yellow; when ignited, it commonly becomes pink; the pink colour may be due to a trace of an intermediate oxide, but is generally attributed to traces of the other rare earths, which generally occur as impurities in cerium salts.

The **salts** are obtained in solution when the ceric oxide is dissolved in acids. The solutions are in every case deep yellow. They are unstable for two reasons: firstly, they tend to hydrolyse, and secondly, they are strong oxidizers, tending to change to cerous salts. The yellow **sulphate,** $Ce(SO_4)_2$, can be obtained by treating ceric oxide with sulphuric acid. The aqueous solution is readily hydrolysed, basic salts being deposited. On the other hand, when a solution containing excess of sulphuric acid is slowly evaporated, a red cerous-ceric sulphate is deposited owing to partial reduction.

The **nitrate** is obtained in solution, when ceric oxide is dissolved in nitric acid, or when cerous nitrate is oxidized with lead peroxide in the presence of dilute nitric acid. It is not possible, however, to obtain the normal salt from the orange solution. A basic salt formed by hydrolysis is the only product obtained upon evaporation.

C. Other Compounds of Cerium.

When ceric oxide is heated in hydrogen, a dark-blue **intermediate oxide,** said to have the composition $2CeO_2.Ce_2O_3$ or Ce_4O_7, is produced. A hydrated form of the same oxide is obtained when a solution containing ceric and cerous salts, in correct proportions, is treated with sodium hydroxide, and comes down as a violet precipitate.

By the action of hydrogen peroxide—or of oxygen—upon ceric compounds, a **peroxide** (CeO_3) is thought to be produced,[1] but its individuality is still a little doubtful.

Hydride. Cerium readily absorbs hydrogen at about 350° C. The dissociation pressure of the product at 450–510° C. is low and practically constant until the hydrogen content exceeds that indicated by the formula CeH_2. Beyond that point the decomposition pressure rises with the hydrogen content. This has been interpreted as showing that the definite hydride, CeH_2, exists, which is capable of holding further hydrogen in solid solution.[2]

Nitride. Cerium combines also with nitrogen to form the nitride, CeN, the colour of which varies between a dark bronze to a bright yellow according to the conditions of formation.

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[1] See L. Pissarjewsky, *Zeitsch. Anorg. Chem.* **31** (1902), 359. Compare E. Baur, *Zeitsch. Anorg. Chem.* **30** (1902), 251.

[2] I. I. Zhukov, *J. Russ. Phys. Chem. Soc.* **45** (1913), 2073; Abstract, *Amer. Chem. Soc. Abstracts,* **9** (1915), 566.

Analytical

Cerous salts give, with sodium hydroxide, a white precipitate of the hydroxide which darkens, through oxidation, on contact with air. Oxalic acid produces, in a cerous solution, a white precipitate of the oxalate, insoluble in excess, thereby enabling the analyst to distinguish cerium from zirconium ; potassium sulphate yields a crystalline precipitate of the double sulphate.

When cerous salts are treated with oxidizing agents, the solution turns orange, owing to the formation of the ceric compounds. But the ceric salts are readily hydrolysed on boiling the solution, insoluble basic salts being produced. The separation of the rare-earth metals from cerium, based upon this fact, has already been referred to (p. 230).

TERRESTRIAL OCCURRENCE AND TECHNOLOGY

The occurrence of cerium in nature, as well as the general uses of cerium, have been briefly referred to in the section on the "rare-earth metals," and will be considered in further detail in connection with thorium, with which cerium is generally associated. There is no occasion, therefore, to discuss the matter at this point.

THORIUM

Atomic weight . 232·15

The Metal

Thorium is a white-grey metal, melting at a high temperature, above 1,700° C. It is heavier than zirconium and cerium, the specific gravity being about 11·0. Thorium is a ductile substance; even samples containing much oxygen possess a certain amount of ductility.

The metal and its compounds are radioactive. The activity of thorium is very much less than that of radium, but thorium preparations often contain some of the decay-products, e.g. mesothorium, which are much more radioactive than thorium itself.

The metal is fairly permanent in the atmosphere at ordinary temperatures, but burns with a bright white flame if heated. It slowly evolves hydrogen from acids, thorium salts being formed, but does not decompose water, even when the temperature is raised.

Laboratory Preparation. The metal can be obtained by heating a mixture of potassium thorium chloride and metallic sodium tightly packed in a closed metal cylinder for 15 minutes.[1] After cooling, the contents are turned out, treated with water to remove the sodium and potassium chloride, when the metallic thorium is left as a glistening powder; but the product obtained in this way always contains oxide, presumably in solid solution. By heating thorium tetrachloride with sodium, preferably *in vacuo*, various workers claim to have prepared thorium practically free from oxide.[2] The metal is obtained as a powder, but can be compressed into a rod or strip either by hammering, or by sintering in an electric vacuum furnace.

Thorium has also been obtained by the electrolysis of a fused mixture of chlorides, but the product contains much oxide.[3]

Compounds

Thorium seems to be tetravalent in all its compounds.

Thorium oxide (*thoria*), ThO_2, is formed when thorium burns in oxygen, or when the hydroxide, nitrate or oxalate is ignited. It is a white, practically infusible substance, which, like zirconium oxide, becomes incandescent when heated; the incandescence is less bright in the case of pure thoria than in the case of thoria containing a small amount of other oxides. The question of incandescence is discussed further in the technical portion. The **hydroxide** is obtained when a thorium salt solution is precipitated with ammonia.

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[1] L. F. Nilson, *Ber.* **15** (1882), 2537.

[2] W. von Bolton, *Zeitsch. Elektrochem.* **14** (1908), 768; D. Lely and L. Hamburger, *Zeitsch. Anorg. Chem.* **87** (1914), 209.

[3] H. von Wartenberg, *Zeitsch. Elektrochem.* **15** (1909), 866.

The oxide formed by ignition of the oxalate, nitrate, sulphate or hydroxide, preferably below 700° C., behaves in a rather curious way towards acids. If warmed with nitric or hydrochloric acid, no dissolution takes place, but, by driving off the excess of acid, a semi-transparent mass is obtained, which although insoluble in acids, breaks up on treatment with pure water, yielding an opalescent colloidal solution. The action of the acid seems to be to form traces of thorium salts on the particles of the oxide. When the mass is treated with water, the thorium ions adsorbed on the oxide surface allow peptization to take place. The opalescent sols are unstable, being easily precipitated by the addition of acids or ordinary salts (e.g. potassium sulphate). Colloidal solutions are also formed when freshly precipitated thorium hydroxide is peptized with hot dilute hydrochloric acid, and the sols thus obtained are clearer and distinctly more stable towards the addition of electrolytes.

Salts. The thorium salts are formed when the ordinary variety of oxide or hydroxide is dissolved in acids. They are heavy colourless substances. The solutions have an even more powerful action in causing the flocculation of negative colloids than do aluminium salts; this would seem to be due to the tetravalent ion, $Th^{\cdot\cdot\cdot\cdot}$. On the other hand, they have a peptizing action on some albuminous substances.[1]

The **sulphate,** $Th(SO_4)_2$, is obtained in the anhydrous state by evaporating the solution of thorium oxide in sulphuric acid to dryness. It is quite soluble in ice-cold water, but, if the solution obtained is preserved for any length of time, a much less soluble hydrated sulphate, $Th(SO_4)_2.9H_2O$, separates out. Advantage of this fact may be taken to purify the salt. Other hydrates[2] are known, the most important being $Th(SO_4)_2.4H_2O$, which is the stable phase at temperatures above 43° C. A sparingly soluble double salt, $Th(SO_4)_2.2K_2SO_4.2H_2O$, is thrown down, when a solution of potassium sulphate is added to thorium sulphate.

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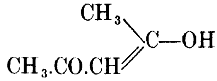
[1] B. Szilard, *J. Chim. Phys.* 5 (1907), 495.

[2] For details of the interesting equilibrium diagram, see H. W. Roozeboom, *Zeitsch. Phys. Chem.* **5** (1890), 201; I. Koppel and H. Holtkamp, *Zeitsch. Anorg. Chem.* **67** (1910), 266; I. Koppel, *Zeitsch. Anorg. Chem.* **67** (1910), 293.

The **nitrate** is very soluble, and therefore somewhat difficult to crystallize. Nevertheless various hydrates can be obtained without the occurrence of hydrolysis. The **chloride,** $ThCl_4$, is formed in solution by dissolving thorium oxide in hydrochloric acid; it is prepared in the anhydrous state by passing chlorine over a mixture of oxide and carbon. The anhydrous chloride is a colourless solid, deliquescent, very soluble and fairly volatile, the vapour density indicating the simple formula $ThCl_4$. A **fluoride,** ThF_4, and complex fluorides, such as **potassium thorifluoride,** K_2ThF_6, corresponding to the zirconifluorides and silicofluorides, are known.

The **oxalate** is of great importance. Like the oxalates of the rare earths it can be precipitated from slightly acid solutions. Unlike the rare-earth oxalates it is distinctly soluble in excess of ammonium oxalate, whilst it differs from zirconium oxalate in being insoluble in oxalic acid.

It is of interest to notice a curious organic derivative of thorium. Acetyl-acetone, which may be written



$$\left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3.CO.CH}\end{matrix}\right\rangle \mathrm{C{-}OH}$$

or $(C_5H_7O_2)H$,

can be regarded as a weak acid; it forms a thorium salt,

$$(C_5H_7O_2)_4Th,$$

which is soluble in chloroform, and which can be distilled *in vacuo* without decomposition.

Analytical

Thorium resembles cerium and zirconium in yielding white precipitates with ammonia, potassium sulphate and oxalic acid. It differs from cerium in that the oxalate precipitate is soluble in ammonium oxalate, and from zirconium in that the oxalate is insoluble in oxalic acid.

The precipitation of the oxalate from acid solution enables us to separate thorium from the majority of ordinary metals. A method of separating thorium from the rare earths has been worked out which depends on precipitation of the warm neutral solutions of the nitrates with hydrogen peroxide in the presence of ammonium nitrate.[1] Thorium is thrown down as peroxide (or a derivative), whilst the rare earths remain in solution. The peroxide is filtered off and ignited, the thorium being weighed as dioxide (ThO_2). Unless ammonium nitrate is present in the solution, the peroxide is precipitated in such a form that it is difficult to ignite it without loss through decrepitation; the ammonium salt makes the precipitate denser, easier to filter, and capable of quiet ignition.

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[1] E. Benz, *Zeitsch. Angew. Chem.* **15** (1902), 303.

Another process often recommended for the estimation of thorium is the method of precipitation with sodium thiosulphate; on adding that reagent to a slightly acid solution, a precipitate of thorium hydroxide and sulphur is produced, which can be filtered off and ignited. But several rare-earth elements and also zirconium, if present, are precipitated—at least partially—with the thorium. The operation requires, therefore, to be combined with other methods of separation.

An interesting method for the estimation of thorium, especially in its ore (monazite sand), depends on the fact that it gives off a radioactive emanation.[1]

TERRESTRIAL OCCURRENCE

Like zirconium and cerium, thorium is found mainly in the acid part of the intrusion. Certain granitic rocks, and particularly the pegmatite veins which constitute the final stages of consolidation, contain the important mineral,

Monazite . . . . . $CePO_4$,

really a phosphate of cerium and the rare-earth metals, but also containing thorium. Where rocks containing monazite have been weathered, the crystals have been carried away by the rivers, but owing to their weight have tended to collect separately from the majority of the lighter sand-particles. "Monazite sands"[2] containing grains of monazite mixed with other heavy constituents of acid rocks, such as zircon, garnet, rutile and the like, are found in Brazil (Bahia, Espirito, and Rio de Janeiro), India (Travancore), Ceylon, and Carolina. In the first three countries, the richest deposits occur on the sea-beach, having been concentrated to a large extent by tidal action. But inland deposits also occur, especially in the beds of streams which rise among rocks containing monazite; these are usually less rich. The Carolina deposits are of a poor character.

The total amount of monazite sand available in the localities named is large. But it must be remembered that, in any "monazite sand," only a certain proportion of the grains (perhaps half) consist of monazite, whilst each monazite crystal may have a thorium content varying from 0 to 30 per cent. Consequently, the coastal sand contains, as a whole, only a small content of thoria. Even after the removal of most of the grains which are not monazite by artificial concentration, the thoria content is usually only about 4–9 per cent.

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[1] H. H. Helmick, *J. Amer. Chem. Soc.* **43** (1921), 2003.

[2] S. J. Johnstone, *J. Soc. Chem. Ind.* **37** (1918), 373R; W. T. Schaller, *U.S. Geol. Surv., Min. Res.* (1919), II, pp. 13, 14.

Monazite varies in colour from pale yellow to dark brown, and the specific gravity varies from 4·7 to 5·2.

Another important thorium mineral is the impure oxide, which invariably contains uranium, and generally many other metals besides; this is known as

Thorianite . . . . $(Th,U)O_2$.

It occurs in Ceylon, in small black cubes, which are considerably heavier than monazite.

The silicate,

Thorite . . . . $ThSiO_4$,

is likewise found in Ceylon, and also in Norway, but is of comparatively infrequent occurrence.

TECHNOLOGY OF THORIUM AND CERIUM [1]

Practically the whole of the world's supply of thorium is derived from the monazite sands of Brazil and Travancore. Since these comparatively rich sources have been developed, the working of the much poorer deposits of Carolina has become unremunerative.

The Brazilian deposits were discovered about 1893, at a time when the new discovery of the incandescent gas-mantle had made thorium a valuable substance. It is stated that for some time the sand was obtained free, being shipped as ballast to Hamburg, where it was immediately sold for about £20 a ton. After some years the Brazilian Government discovered the real value of the "ballast," but a Hamburg firm secured a monopoly of the mining rights, paying a royalty of 50 per cent. to the Brazilian Government. In 1909, the Travancore deposits were discovered, but, as the capital required to work them was not forthcoming from British sources, the control of this source also passed into German hands.

Just before the outbreak of war in 1914, practically the whole of the productive thorium deposits and almost the whole manufacture of the thorium salts needed for the gas-mantle industry were under German control. There was a great shortage of thorium nitrate in England in 1915. However, works for treating the Indian monazite were soon established in this country, and the successful production of thorium nitrate began; arrangements were made later to work the Ceylon deposits.[2] Meanwhile, the thorium salt industry in the United States had expanded considerably, depending on the Brazilian sand as raw material.

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[1] S. J. Johnstone, *J. Soc. Chem. Ind.* **35** (1916), 811; **37** (1918), 373R. See also G. Martin, "Industrial Chemistry" (Crosby, Lockwood), Section **77**; S. J. Johnstone, "The Rare-Earth Metals" (Longmans, Green), Chapter VII.

[2] *J. Soc. Chem. Ind.* **36** (1917), 1203.

Since the monazite sand, as found on the coast, only consists of a small proportion of monazite grains, it is usually " concentrated " near to the spot where it is found, so as to avoid burdening the ships with the valueless constituents. Advantage may be taken of the difference in gravity of the different constituents to obtain separation, the Wilfley table (described in Vol. I, page 123) being frequently employed. Magnetic separation has also been used with success for the concentration of monazite sands.

The details of the manufacture of thorium nitrate from the concentrate as practised in Europe are kept secret.[1] The outline of the process commonly employed, however, is understood to consist in the dissolution of the monazite sand (previously ground, if necessary) in hot concentrated sulphuric acid. The phosphates are dissolved by the concentrated acid, but, when the mass is afterwards extracted with water, and the acid is partly neutralized with magnesia, the thorium phosphate is reprecipitated. If enough magnesia were at once added for complete neutralization, cerium and all the rare-earth metals present would be thrown down with the thorium ; actually, however, the magnesia is added in small quantities at a time, and all the thorium phosphate is found in the first fractions of the precipitate, together with some rare-earth metals ; the majority of the rare earths are separated with the later fractions of the precipitate. The impure thorium phosphate may then be dissolved in concentrated hydrochloric acid, and oxalic acid is added, which throws down a precipitate of thorium oxalate. If the acidity is correct, comparatively little of the rare earths is precipitated. When the oxalate is warmed with sodium carbonate solution, the thorium is dissolved and a further portion of the cerium earths still present are left behind as an insoluble double carbonate. The thorium can then be precipitated once more with oxalic acid, and the oxalate converted to the sulphate; further purification is effected through fractional crystallization of that salt ; finally it is converted to pure thorium nitrate.

The thorium nitrate required for mantle making must be quite free from phosphates and from the rare earths. Many attempts have been made to devise cheaper methods of eliminating phosphorus, as the cost of the oxalic acid needed for the process just described is considerable. In one process,[2] the monazite is heated with coke, lime and fluorspar in the electric furnace, when the phosphorus volatilizes away. The product is washed to remove lime, and then dissolved in hydrochloric acid, after which the thoria is precipitated with sodium thiosulphate.

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[1] Certain stages in the American process are described in *Met. Chem. Eng.* **21** (1919), 500.

[2] C. Baskerville, *8th Int. Cong. App. Chem.* (1912), II, 12.

Manufacture of the Welsbach Gas-Mantle. The starting point of the gas-mantle is usually a mantle woven of ramie fibre, which gives a product very much more efficient than cotton; artificial silk is also used.[1] The ramie mantles require to be soaked well in dilute acid, so as to remove any mineral impurities present, and then in dilute ammonia, which probably serves to remove grease. They are dried in hot air, and afterwards "impregnated" in a solution containing thorium nitrate with small amounts of cerium, beryllium and magnesium nitrates. The mantles are then dried again, and the ramie is "burnt off," leaving in the place of the original mantle an "ash skeleton" consisting of thoria (with small amounts of ceria, beryllia and magnesia), but having the form of the original ramie. The skeleton is strengthened by immersion in a collodion solution containing camphor, and is then strong enough to bear transport in boxes. The collodion is, of course, "burnt off" when the mantle is fitted by the domestic consumer on to his burner.

The mantle, when it is finally used as an incandescent material, consists essentially of thoria with 1 per cent. of ceria in solid solution. The beryllia and magnesia are present in smaller quantities, and serve only to increase the strength. When the non-luminous Bunsen flame of the burner is lighted, the mantle becomes extremely hot, and commences to give out light.

Theory of the Efficiency of the Welsbach Mantle. It is found that mantles consisting of pure thoria give a much less bright light than those containing 1 per cent. ceria, but that any further increase of the ceria-content decreases the luminosity, although a rather larger proportion of ceria is employed with advantage in the mantles used for the high-pressure burner.[2]

It is interesting to inquire why this particular mixture is more efficient as a light-producer than any other material which will withstand the temperature. It is sometimes stated that a Welsbach mantle will produce no more light than a similar mantle made of any other material held at the same temperature; its special virtue—according to this view—lies in the fact that it actually attains a higher temperature when placed within the flame than do other substances.[3] The high temperature reached by the Welsbach mantle is mainly due to the fact that thoria is a highly transparent substance, and accordingly does not emit rays (visible or otherwise) to the same extent as would a non-transparent or *black* substance. Since the production of any rays necessarily causes the radiant material to cool, any substance which does not give off rays to the full extent will clearly become hotter than a black substance placed in the same flame. But just because thoria itself is comparatively non-radiant, a pure thoria mantle will provide comparatively little light, in spite of its high temperature. The function of the ceria is to cause the mantle to emit "visible" rays; the emission is at a maximum in the blue region of the visible spectra. If too much ceria is added, the emission spreads to other parts of the spectrum, and the proportion of invisible rays increases; at the same time, the temperature becomes lower again owing to the increased radiation. Hence the addition of ceria in small quantities increases the efficiency, but larger quantities depress it.[1]

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[1] E. L. Knoedler, *Met. Chem. Eng.* **15** (1916), 635.

[2] E. Stern, *Zeitsch. Angew. Chem.* **26** (1913), 1. 806.

[3] F. Haber, *J. Soc. Chem. Ind.* **33** (1914), 51.

We can put the matter very shortly as follows. The thoria mantle reaches a higher temperature than a black body exposed to the same flame, whilst the small ceria content allows it to emit more visible light than a black body would emit, even at the same temperature. The Welsbach mantle has an abnormally high emissive power within the visible region, and an abnormally low emissive power outside it.

It is quite possible that the mantle substance aids catalytically the combination of the coal gas and oxygen, and that the combustion, taking place close to its surface, causes it to reach a higher temperature than would be reached by a similar mantle without catalytic activity.[2]

Other Uses of Thorium Compounds. Curiously enough, thoria, besides its use in gas-mantles, is employed to a small extent in the tungsten filaments of electric bulbs; the main function of the thoria (which will be discussed in the section on tungsten) appears to be the control of grain growth in the filament.

Thorium salts are of some slight importance in tropical medicine; they are found to have an agglutinating and bactericidal action on certain pathogenic organisms, including those that cause cholera and dysentery.[3]

Uses of Cerium and other Bye-products of the Monazite Industry. Cerium and the rare earths occur in monazite in larger quantities than thorium, and the problem of finding a use for the relatively large quantities of these bye-products has at different times exercised the minds of those connected with the thorium industry. The fact that 1 per cent. of ceria is required in the mantle skeleton only calls for the consumption of a small fraction of the ceria available.

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[1] H. E. Ives, E. F. Kingsbury and E. Karrer, *J. Franklin Inst.* **186** (1918), 401, 585; H. Rubens, *Ann. Phys.* **20** (1906), 593.

[2] Compare E. K. Rideal and H. S. Taylor, "Catalysis" (Macmillan), p. 124.

[3] A. Frouin and D. Roudsky, *Comptes Rend.* **159** (1914), 410; A. Sartory and P. Bailly, *Comptes Rend.* **172** (1921), 1257.

A considerable amount of the residue containing cerium and the rare-earth metals is used in the production of pyrophoric alloys. The metals are precipitated with oxalic acid and the oxalates are converted to hydroxides, which are dissolved in hydrochloric acid and dehydrated in a silica vessel in a current of hydrogen chloride. The mixed chlorides are then fused in an iron or plumbago crucible and electrolysed at 15–20 volts, a carbon anode being employed.[1] An alloy of very varying composition is obtained, known as **Mischmetall**, which consists mainly of cerium, lanthanum, praseodymium and neodymium, with much smaller quantities of the other elements. The percentage of cerium is often about 40–50 per cent., that of lanthanum may perhaps be about 25 per cent.; there is usually about 15 per cent. of praseodymium, neodymium and samarium, and smaller amounts of iron and other metals. This mixture is then further alloyed with 30 per cent. of iron to give the hard pyrophoric material, known as **ferro-cerium**, used as a "flint" in automatic cigarette-lighters and gas-lighters. Other pyrophoric alloys containing Mischmetall along with zinc and magnesium are said to be made in Germany.

Another use of Mischmetall is that of a deoxidizer. It has been employed as an addition to copper, just before pouring, the copper being rendered free from gases, stronger and more ductile by the treatment. Ferro-cerium has also been tried with success as an addition to cast iron.[2] Cerium steels are said to have been made at several steelworks in France.

Mischmetall has proved of value as a reducing agent in the preparation of other metals which are difficult to reduce, for instance vanadium.

An appreciable amount of cerium is also used for impregnating arc carbons. It is usually applied as the fluoride. Apart from this, quite small quantities of cerium are used in dyeing, and in photography, whilst cerium salts are said to be employed in remedies for sea-sickness. Cerium is used in certain kinds of optical glass. In war-time a considerable amount of cerium is required for tracer-bullets and searchlights.[3]

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[1] A. Trillat, *Bull. Soc. d'Enc.* **131** (1919), 60. See also H. Kellermann, "Die Ceritmetalle und ihr Legierungen" (Knapp).

[2] A. Hirsch, *Trans. Amer. Electrochem. Soc.* **37** (1920), 359.

[3] *J. Soc. Chem. Ind.* **40** (1921), 40R. Also S. J. Johnstone, *J. Soc. Chem. Ind.* **37** (1918), 376R.

Like many metals with two sets of salts, cerium salts are powerful catalysts, and have been employed in certain processes as oxygen carriers; they have been tried as "driers" for oil.

In addition to cerium, a certain amount of mesothorium 1 is obtained as a by-product of the mantle industry, and this has been employed as a source of radioactivity. If a little barium chloride is added to the solution of monazite in sulphuric acid, the barium sulphate produced carries down all the radium present, and also the mesothorium 1, which is an isotope of radium. The separation from barium is conducted by the ordinary method used for concentrating radium.

The period of half-change of mesothorium 1 is only about 5½ years, much shorter than that of radium. For this reason, preparations containing mesothorium can be made which are much more active than pure salts of radium; but they must, of course, be less permanent, losing half the activity due to mesothorium in 5½ years, three-quarters of it in 11 years, and so on. Technical mesothorium preparations generally contain much radium as well. It is hoped that they will come to be employed largely in luminous paints—used for instruments which require to be read in the dark; the general employment of mesothorium for such purposes would liberate true radium preparations for medical uses, for which they are badly needed.

GROUP VA

Vanadium	51·0
Niobium (Columbium) . .	93·1
Tantalum	181·5
Eka-tantalum . . .	230

The elements of Group VA have a maximum valency of five, and form stable oxides of the type M_2O_5; but, like most metals of high maximum valency, compounds are also known corresponding to lower oxides. The higher oxides are acidic rather than basic, the lower oxides basic rather than acidic. A connection exists between the pentavalent elements of this group and the pentavalent elements of Group VB; many of the vanadates, including the complex vanadates, are isomorphous with the corresponding phosphates.

The elements themselves are hard and take a fine polish. As in the case of the two previous groups, the metal, when in a compact form, often displays a simulated nobility, caused by the existence of an adherent oxide-film on the metal. A good example of this "apparent nobility" is afforded by tantalum, which is actually used as a substitute for platinum. Tantalum and niobium resemble aluminium in showing "valve action," when employed as anodes, and it is interesting to note that antimony and bismuth, two members of Group VB, also display valve action.

"**Eka-tantalum,**" the last metal belonging to the group, has never been prepared in a visible quantity, and merits no special description. It is a radioactive element, which is believed to exist in certain eight-year-old preparations of Uranium X examined by Soddy.[1] It is probably the product of decay of Uranium Y, and is of special interest as being the parent of actinium. Another radioactive element, "**uranium X_2**," is isotopic with eka-tantalum, and has consequently the same chemical properties but a different atomic weight (234); this element has a very short period, and exists therefore only in very minute quantities in uranium preparations.

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[1] F. Soddy and J. A. Cranston, *Proc. Roy. Soc.* **94** [A] (1918), 384.

VANADIUM.

Atomic weight 51·0

The Metal

Our knowledge of elemental vanadium, like that of elemental titanium, is limited owing to the difficulty of obtaining the element free from oxygen and nitrogen. In both cases the substance believed by the early chemists to be the element was proved subsequently to be the nitride. True vanadium appears to be a white-grey lustrous substance, very hard, and somewhat brittle ; it takes an unusually good polish, and, on the whole, it resembles high carbon steel in appearance and physical properties. Like the members of the last group, it fuses at a high temperature (1,720° C.), only just below the melting-point of platinum. The shrinkage patterns produced on the free surface of a vanadium ingot suggest that the metal crystallizes from the fused state in the hexagonal system [1] ; but X-ray investigation at ordinary temperatures indicates that the system is cubic, the atoms being arranged on a centred cube lattice.[2]

The chemical properties of vanadium vary considerably with the state of division in which it exists. Finely divided vanadium combines readily with oxygen and with nitrogen when heated in these gases, and is said to burn when introduced into a flame. On the other hand, the compact and polished metal can be heated in air with only superficial oxidation, the colour becoming brass-coloured, owing, no doubt, to a thin oxide film. At ordinary temperatures polished vanadium can remain in air for a long time without undergoing appreciable change ; presumably this is due to a protective film which is at low temperatures too thin to be visible. Possibly for the same reason the element is not very readily attacked by reagents, although, when once in the combined state, vanadium is only with difficulty reduced to the elemental condition. Vanadium precipitates gold and silver from solutions of their salts, but it does not evolve hydrogen from dilute hydrochloric or sulphuric acids, or from aqueous solutions of caustic alkali. Nevertheless, it is dissolved by hydrofluoric acid, and by fused caustic soda, hydrogen being in each case evolved. Oxidizing acids, like nitric and strong sulphuric, also attack vanadium.

[1] See L. Weiss and O. Aichel, *Lieb. Ann.* **337** (1904), 382.

[2] A. W. Hull, *J. Franklin Inst.* **193** (1922), 200.

Whilst the metal has no action upon water at ordinary temperatures, it is oxidized at high temperatures even by traces of water vapour.

Laboratory Preparation. No very easy method of obtaining metallic vanadium exists. When the pentoxide is reduced with carbon in the electric furnace, the product contains either carbon or oxygen, according to the proportions of the two reagents employed. If sufficient carbon is present, the main product may be the silvery carbide (VC). If the reducing agent employed is aluminium or potassium, the resulting material is liable still to contain oxygen. If a mixture of the carbide and the oxide, in carefully adjusted proportions, is heated, the two non-metals are largely, but not completely, eliminated.[1]

A slow method of obtaining vanadium depends on passing a current of dry hydrogen over the dichloride (VCl_2) strongly heated in a porcelain tube; the hydrogen must be absolutely dry, since the smallest traces of water will cause the oxidation of the metal.

A much quicker method is to heat the pentoxide with *Mischmetall*, the alloy of cerium and other rare metals which has already been referred to. It may seem curious that so unusual a reducing agent should be employed, but it must be remembered that mischmetall is composed of highly reactive metals, which give out more heat when they are oxidized than does aluminium, which are less volatile than potassium, and which do not easily alloy with vanadium at a high temperature. It is doubtful whether any other reducing agent possesses the same qualifications. When the mixture of powdered mischmetall and vanadium oxide is heated in a magnesia crucible, a very violent "thermite" reaction occurs, the cerium metals being oxidized almost instantaneously with a great evolution of heat; the vanadium produced is completely molten and, after cooling, is obtained as a good button.[2] Analysis has shown the metal, prepared in this way, to contain about 99·7 per cent. of vanadium.

Compounds

At least four oxides of vanadium exist, V_2O_5, VO_2, V_2O_3 and VO. In addition, a lower oxide V_2O has been described, although its identity is doubtful; whilst compounds corresponding to a peroxide (V_2O_7) have been isolated, although the oxide itself is unknown. The four important oxides possess basic properties, and form salts with acids which are recognizable by their colour in solution, although they cannot always be obtained in the solid state on account of hydrolysis. As is usually the case, the higher oxides are less strongly basic than the lower oxides. The two highest oxides have well-marked acidic properties, and form salts with alkalis; the vanadates, formed from the highest oxide (V_2O_5), present a close analogy to the phosphates.

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[1] Compare O. Ruff and W. Martin, *Zeitsch. Angew. Chem.* **25** (1912), **49.**

[2] W. Muthmann, L. Weiss and R. Riedelbauch, *Lieb. Ann.* **355** (1907), **59.**

As is usual with metals of variable valency, the salts of vanadium display selective absorption for light of certain wave-lengths within the range of visibility; in other words, they are coloured. Very remarkable colour-changes are observed when the solution obtained by dissolving the highest oxide in sulphuric or hydrochloric acid is reduced with zinc. Similar colour changes are seen when a solution in hydrochloric acid is placed in the cathodic compartment of an electrolytic cell divided into two compartments by a porous pot, reduction being carried out by means of the electric current. The course of the reduction depends on the cathode material. Using a lead cathode, four stages of reduction can be distinguished, each stage being marked by a different coloration. The original solution, containing a salt of V_2O_5, is yellow; upon reduction the colour changes through green to blue, which is the colour of the salt of VO_2; further reduction at ordinary temperatures causes a green coloration, due to a salt of V_2O_3, but above 90° C. reduction proceeds still further, a salt of VO being produced, which gives a violet-blue tint to the solution.[1]

The colours of the different solutions are sometimes ascribed to the ions $V^{\cdot\cdot\cdot\cdot\cdot}$, $V^{\cdot\cdot\cdot\cdot}$, $V^{\cdot\cdot\cdot}$, and $V^{\cdot\cdot}$, although it is very doubtful whether most of these ions have any real existence in the solutions, since hydrolysis occurs, and complex cations containing oxygen are probably formed. The colours and important properties of the four types of vanadium salts are shown in tabular form on page 274.

A. Compounds of Pentavalent Vanadium (Vanadic Compounds).

Salts of vanadic oxide (V_2O_5) are formed when any of the lower salts of vanadium are oxidized with potassium permanganate in the presence of acid. The oxide itself is produced when any lower oxide—or the metal itself—is treated with nitric acid, and the product evaporated to dryness. It is more conveniently prepared by ignition of ammonium vanadate in air at 440° C. The oxide is met with in different forms, and the colour may be yellow, red, or grey.[2] The yellow amorphous form is the one usually obtained by heating ammonium vanadate. It fuses without decomposition

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[1] S. Fischer, Junr., *Trans. Amer. Electrochem. Soc.* 30 (1916), 175.

[2] W. F. Bleeker, *Met. Chem. Eng.* 8 (1910), 666.

Valency.	Series of Salts.	Colour of Solution.	Properties.
[illegible]	Salts of V_2O_5 (Vanadic salts)	Yellow, due to $V^{\cdot\cdot\cdot\cdot\cdot}$ or, more probably $[VO_2]^{\cdot}$ or $[VO]^{\cdot\cdot\cdot}$	Mild oxidizer. Oxidizes sulphurous acid.
4	Salts of VO_2 (Hypovanadic salts)	Blue, due to $V^{\cdot\cdot\cdot\cdot}$ or perhaps $[VO]^{\cdot\cdot}$	Mild reducer. Reduces potassium permanganate.
3	Salts of V_2O_3 (Vanadious salts)	Green, due to $V^{\cdot\cdot\cdot}$ or perhaps $[VO]^{\cdot}$	Strong reducer. Precipitates metallic silver from silver salts.
2	Salts of VO (Hypovanadious salts)	Lavender, perhaps due to $V^{\cdot\cdot}$	Very powerful reducer. Solutions spontaneously evolve hydrogen on warming.

when heated in air, and the fused oxide crystallizes on cooling, yielding a distinctly crystalline mass, described by some authors as grey and by others as red. The probable cause of this disagreement is that fused vanadium pentoxide is very active, attacking even platinum; the colour of the liquid is yellow-red when pure, but the merest trace of organic matter causes it to darken owing to the formation of VO_2.

A red curdy form of the pentoxide is precipitated by the action of acids on a solution of a soluble vanadate. Another "red amorphous" form is produced when ammonium vanadate is heated, and the residue treated with nitric acid and again ignited. The product on cooling is hygroscopic, and absorbs water from the air, becoming red. When shaken with water, it appears to dissolve, forming what is evidently a colloidal solution, since it is flocculated by the addition of salts or acids.

An effective method of preparing a colloidal solution of vanadium pentoxide is to grind ammonium vanadate with dilute hydrochloric acid, and to wash the reddish-brown product (vanadium pentoxide) on a filter with water, until the wash-water passing through the filter-paper begins to be coloured. At this point, the whole contents of the filter are removed into pure water; they dissolve readily, yielding a clear red-yellow liquid.[1] On electrolysis the particles move towards the anode—a fact which shows that they are negatively charged.

The colloidal solutions of vanadium pentoxide are of quite special interest owing to the fact that the particles appear to have a crystalline character.[2] Immediately after preparation, the particles seem to be more or less round, but after storing for some months at ordinary temperature, or even after heating for a short time at 90–100° C., the liquid acquires optical properties which seem to indicate that the particles are crystalline. An ultramicroscopic study of the liquid at this stage suggests that the particles have grown to be rod-shaped. In addition, the liquid when stirred exhibits a " silkiness " similar to that produced when a suspension of minute lead iodide crystals in water is stirred; this silkiness is due to the fact that all the little crystals in any given part of the liquid turn in such a way that their longer axes are parallel to the direction in which the water is moving. The viscosity of the " sol " increases with the duration of heating, and if the heating is continued sufficiently long, the liquid may gelatinize.

Vanadium pentoxide possesses both basic and acidic properties. It dissolves in concentrated sulphuric, hydrochloric and hydrofluoric acids, yellow solutions being obtained. It is not easy to isolate salts from these solutions; the solution in hydrochloric acid, for instance, evolves chlorine upon evaporation. In other cases complete hydrolysis occurs, but in various instances basic salts can be obtained. For instance, a solution of vanadium pentoxide in concentrated sulphuric acid, heated for some time, deposits a reddish **sulphate** having the composition $[VO]_2(SO_4)_3$ (possibly containing combined water). The solution in hydrofluoric acid yields, upon the addition of potassium fluoride, yellow crystals of the **double fluoride** $2KF.[VO_2]F$.

The **vanadates**, which are combinations of the pentoxide with basic oxides, are better defined substances. **Ammonium metavanadate** (NH_4VO_3) is formed when vanadium pentoxide is dissolved in aqueous ammonia, and is obtained in colourless crystals when the solution is evaporated. It is almost insoluble in excess of ammonium chloride, and therefore is brought down as a precipitate wherever a concentrated solution of a vanadate is saturated with ammonium chloride. The metavanadates of many metals, such as barium, lead and silver, are insoluble yellow precipitates obtained by the interaction of ammonium metavanadate and a solution of a salt of the metal in question.

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[1] W. Biltz, *Ber.* **37** (1904), 1098.

[2] W. Reinders, *Koll. Zeitsch.* **21** (1917), 161; *Proc. Amst. Acad.* **19** (1916), 189. Compare the views of H. Diesselhorst and H. Freundlich, *Phys. Zeitsch.* **16** (1915), 419; H. Freundlich, *Zeitsch. Elektrochem.* **22** (1916), 27. These authorities think that there is no true crystal formation. See also H. R. Kruyt, *Proc. Amst. Acad.* **18** (1916), 1625; H. Zocher, *Zeitsch. Phys. Chem.* **98** (1921), 293.

When a solution of ammonium metavanadate is acidified with acetic acid, the liquid becomes yellow owing to the formation of an anhydro-salt, **ammonium tetravanadate**, $2NH_4VO_3.V_2O_5$, which can be obtained in the solid state by evaporation *in vacuo*. On the other hand, two series of salts more basic than the metavanadates are known. **Sodium pyrovanadate** ($Na_4V_2O_7$) and **orthovanadate** (Na_3VO_4) are obtained when vanadium pentoxide is fused with the theoretical quantities of sodium carbonate and the products crystallized from water. The pyrovanadates and orthovanadates are less stable than the metavanadates, and are chiefly of interest on account of the analogy presented to the pyrophosphates and orthophosphates. It is found that the various metavanadates, pyrovanadates and orthovanadates are frequently isomorphous with the metaphosphates, pyrophosphates and orthophosphates containing the same amount of water of crystallization. The pyro- and orthovanadates of the heavy metals (e.g. silver, lead, etc.) are in most cases insoluble, and can be obtained as yellow or reddish precipitates by double decomposition from the sodium salts. The vanadates of mercury, lead, copper and iron can be fused at about 600° C. and set to extremely hard masses on cooling.

When the vanadates are decomposed with acids, hydrates of vanadium pentoxide are produced, as already mentioned. The product varies in appearance according to the conditions of preparation, and the earlier chemists assigned special names and formulæ to various forms. For instance, the brown precipitate obtained by the action of acids upon a tetravanadate has been considered to be "pyrovanadic acid," $H_4V_2O_7$, but there appears to be no very convincing reason for regarding it as a definite compound.

The so-called "metavanadic acid," often regarded as HVO_3, deserves special mention. It is formed from the metavanadates of copper, zinc, or other heavy metals. A convenient method of preparation consists in adding to a solution of copper sulphate containing excess of ammonium chloride a solution of ammonium vanadate, until a permanent precipitate begins to come down, after which the liquid is heated at 75° C. The metavanadic acid is brought down in glittering gold spangles.[1] Its fine lustre has led to the name of "vanadium bronze." According to some authorities,[1] the "vanadium bronze" is really an ammonium vanadate, not "metavanadic acid." It certainly appears to contain traces, at least, of ammonia.

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[1] B. W. Gerland, *Ber.* 9 (1876), 872.

B. Compounds of Tetravalent Vanadium (Hypovanadic Compounds).

Hypovanadic oxide, VO_2, is formed when a mixture of the higher and lower oxides (V_2O_5 and V_2O_3) is strongly heated; it is said to be formed also upon the electrolysis of the molten pentoxide. It is a blue lustrous substance, which, unlike the pentoxide, is extremely infusible. A hydrated form, obtained by precipitation of the corresponding salts by means of sodium carbonate, is a grey precipitate, becoming dark when dried. Hypovanadic oxide possesses both basic and acidic properties, and dissolves in acids and in alkalis. The solutions in acids have a bright blue colour, due to hypovanadic salts. These blue solutions can also be obtained by the mild reduction of vanadic salts, for instance by the action of sulphur dioxide upon a solution of vanadium pentoxide in sulphuric acid. Sulphur dioxide reduces vanadium to the hypovanadic condition, but not further. No normal salts of the type $V(SO_4)_2$ are known, but a **basic sulphate,** $[VO]SO_4$ (usually known as "vanadyl sulphate") is thrown down as a blue powder when the blue solution of VO_2 in sulphuric acid is heated for some time. An example of an insoluble hypovanadic salt is provided by the bluish-green phosphate, which is produced by precipitation.

Solutions of hypovanadic oxide in caustic alkalis are deep brown and contain **hypovanadates.** Potassium hypovanadate, $K_2O.4VO_2.7H_2O$, can be obtained in the solid state by the crystallization of such a solution, and is a reddish-brown substance. The hypovanadates of the heavy metals are mostly insoluble, almost black, powders, obtained from the potassium salt by precipitation.

C. Salts of Trivalent Vanadium (Vanadious Compounds).[2]

Vanadious oxide, V_2O_3, is obtained when the pentoxide is heated in hydrogen. It is a black powder, almost infusible, which readily absorbs oxygen when exposed to the air. The hydrated oxide, prepared by precipitation of the salts with ammonia, is a greenish gelatinous precipitate, which is also easily oxidized. As usually prepared, the anhydrous oxide is only very slowly dissolved by acids, but the salts corresponding to it can readily be obtained in solution by the reduction of the salts of higher oxides. Magnesium is a particularly useful reducing agent for the purpose, because it will reduce the salts of V_2O_5 to the salts of V_2O_3, but the reduction will not proceed further,[1] and the solution will remain free from salts of VO. Solutions of the vanadious salt possess a green colour in the presence of free acid; in the absence of excess of acid, the solutions are usually of a chocolate colour, no doubt owing to hydrolysis. If a cold solution of hypovanadic oxide (VO_2) in sulphuric acid is placed in the cathodic compartment of an electrolytic cell provided with a lead cathode, and if a current is passed through the cell, the blue colour gradually changes to green, and finally an **acid vanadious sulphate,** $V_2(SO_4)_3.H_2SO_4.12H_2O$, separates in minute green crystals. The anhydrous **normal sulphate** $V_2(SO_4)_3$ is obtained by dissolving the green acid sulphate in a little water, adding a little sulphuric acid, and heating at 180° C. in a stream of carbon dioxide; a yellow precipitate comes down, and should be separated by filtration through porous porcelain, quickly washed with water, alcohol and ether, and dried *in vacuo* over sulphuric acid. Possibly on account of the high temperature of formation, it is almost insoluble in water; but it dissolves in hot dilute sulphuric acid, giving a green solution.[2]

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[1] A. Guyard, *Bull. Soc. Chim.* 25 (1876), 356.

[2] Some writers rather illogically speak of these as "Vanadi-salts."

All vanadious salts, like the corresponding titanous salts, are powerful reducing agents. Vanadious oxide has no acidic character and is undissolved by alkalis.

D. Compounds of Divalent Vanadium (Hypovanadious Compounds).

Hypovanadious oxide, VO, is formed when the higher oxides are heated very strongly out of contact with the air with a strong reducing agent, such as potassium. The best method of preparing it is by passing hydrogen gas loaded with the vapour of the volatile oxy-chloride ($VOCl_3$) through a hard-glass tube containing charcoal, heated to redness in a combustion furnace. The hydrogen removes the chlorine, and the oxide, VO, is deposited amongst the charcoal. It is a grey substance of metallic appearance, which, like the nitride, was thought, when first produced, to be metallic vanadium. It melts only at a very high temperature

Hypovanadious oxide dissolves in acids, yielding violet-blue solutions which contain hypovanadious salts. The same solutions may be obtained upon the reduction of vanadic compounds, either by addition of zinc to the acidified solution or by electrolysis. They must be protected from the air, since they absorb oxygen very readily. In fact, when the solutions are heated, they actually evolve hydrogen. They are very powerful reducing agents and reduce salts of copper, tin, silver and gold to the metallic condition; the solutions bleach certain organic colouring substances such as indigo or litmus. On account of the great tendency of hypovanadious salts to become oxidized the isolation of the solid substances presents difficulty. But by evaporation of the solution *in vacuo*, the **sulphate,** $VSO_4.7H_2O$, has been obtained in violet crystals, isomorphous with ferrous sulphate, $FeSO_4.7H_2O$.

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[1] According to H. E. Roscoe and C. Schorlemmer, "Treatise on Chemistry" (Macmillan), Vol. II.

[2] A. Stähler and H. Wirthwein, *Ber.* **38** (1905), 3978.

E. Highly Oxidized Compounds of Vanadium.

Certain compounds of vanadium corresponding to a higher state of oxidation than V_2O_5 are formed when hydrogen peroxide is added to a solution of a metavanadate. A yellow solution is produced, which contains a pervanadate. In some cases the solid body can be isolated; for instance, on adding alcohol to a solution containing potassium metavanadate, hydrogen peroxide and sulphuric acid, **potassium pervanadate,** KVO_4, is precipitated as a yellow powder, since it is comparatively insoluble in water containing alcohol. The corresponding **pervanadic acid,** HVO_4, is deposited in yellow crystals from a solution of vanadic oxide (V_2O_5) in sulphuric acid to which hydrogen peroxide has been added; but the anhydrous peroxide (V_2O_7) is unknown. The solutions of all the pervanadates have a deep orange-yellow colour, which is much more intense than the faint yellow of the vanadates. The solutions are unstable, readily evolving oxygen. In the presence of hydrogen peroxide and free acid, they lose oxygen particularly readily; the solution, under these conditions, becomes blue, indicating that the vanadium is reduced to the tetravalent condition.[1]

F. Miscellaneous Compounds.

Chlorides of Vanadium.[2] It is impossible to obtain the various chlorides of vanadium by concentrating the solutions of the oxides in hydrochloric acid. Hydrolysis always occurs, and the hydroxide, or at best a basic chloride, is precipitated. The preparation of vanadium chlorides, therefore, must be accomplished in a "dry way." When pure dry chlorine gas is passed over vanadium pentoxide heated in a hard-glass tube at a dull red heat (below the melting-point of the pentoxide) the **oxychloride,** $VOCl_3$, is produced almost quantitatively, oxygen being turned out by chlorine. It can be condensed as a yellow liquid in a cool receiver. When the oxychloride is heated with sulphur for twelve hours in a reflux apparatus, the oxygen is eliminated and vanadium

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[1] V. Auger, *Comptes Rend.* **172** (1921), 1355.

[2] O. Ruff and H. Lickfett, *Ber.* **44** (1911), 506.

trichloride, VCl$_3$, remains; excess of sulphur can finally be removed by distillation in a stream of carbon dioxide, and the trichloride is left behind as a pink or violet crystalline crust. It is deliquescent, and reacts with water to give a chocolate-coloured solution which becomes green (like all vanadious salt solutions) on the addition of acid.

When heated in a stream of nitrogen, the trichloride decomposes to a mixture of **dichloride,** VCl$_2$, and **tetrachloride,** VCl$_4$. The latter, like the tetrachlorides of tin and titanium, is a volatile liquid and distils off, whilst the dichloride, which is a scarcely volatile solid, remains behind in green flakes. The dichloride thus prepared seems to be fairly stable (although information on this point is contradictory); but when exposed to air, it absorbs water and oxygen, giving the chocolate-coloured liquid referred to above. The tetrachloride can be obtained, as just stated, by the spontaneous decomposition of the trichloride, but a better yield is obtained by passing chlorine over the heated trichloride. It is a brown liquid, which yields, with water, a solution having the blue coloration typical of all tetravalent vanadium salts.

Vanadium nitride. It has already been mentioned that vanadium unites with nitrogen when heated in a current of that gas, but the reaction takes many hours to complete even at a bright red heat. A blackish powder is obtained, which finally reaches the composition V_2N and ceases to take up further nitrogen.[1] The dissociation-pressure of the nitride thus obtained is very low, less than 0·2 mm. at 1,203° C.[2] Nitrides have also been obtained by the action of ammonia gas upon the pentoxide of vanadium at a high temperature; according to Roscoe,[3] the resultant compound has a composition VN. The same authority states that a higher nitride, VN$_2$, is obtained by the action of ammonia on the trichloride, the residue obtained being heated to expel ammonium chloride. Muthmann considers the individuality of these two nitrides to be somewhat doubtful.

Analytical

The numerous colour-changes which accompany the reactions of vanadium compounds in solution are useful in detecting the presence of the metal. Vanadium compounds in the fully oxidized (vanadic) condition possess, in the presence of acids, a yellow colour, but when they are reduced with zinc, it becomes blue. Caution is necessary, however, in drawing conclusions, for the compounds of several other metals, e.g. niobium, tungsten and molybdenum, also give a blue colour with zinc. Tannic acid gives a black coloration ("vanadium ink") when added to the solution of a metavanadate, but, here again, salts of another metal (iron) produce a similar coloration. The addition of ammonium sulphide to an ammoniacal solution containing vanadium yields a fine cherry-red coloration due to a complex sulphide.

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[1] W. Muthmann, L. Weiss and R. Riedelbauch, *Lieb. Ann.* 355 (1907), 93.

[2] See R. E. Slade and G. I. Higson, *Brit. Assoc. Rep.* 83 (1913), 451.

[3] H. E. Roscoe and C. Schorlemmer, "Treatise on Chemistry" (Macmillan), Vol. II.

The quantitative separation of vanadium from most other metals depends on the acidic character of the highest oxide (V_2O_5) and the insolubility of the lead and mercury salts. The vanadium must first be oxidized to the vanadic condition, if not already present in that condition, by the addition of potassium permanganate, or by fusion with potassium nitrate, according to circumstances. The solution is then made weakly alkaline, so that the salt is present as a vanadate, filtered from any insoluble hydroxides and treated with lead acetate. The vanadium is precipitated as the insoluble basic lead vanadate, and is thus separated from most other metals. The precipitate has not a very constant composition, and it is best therefore to dissolve it in nitric acid, separate the lead as sulphate by the addition of sulphuric acid and alcohol, and evaporate the filtrate to dryness; the residue, after ignition for some time at a faint red heat, is weighed as vanadic oxide (V_2O_5). A quicker process is to precipitate the vanadium by means of mercurous nitrate, instead of lead acetate. The mercury vanadate can be ignited direct to yield the oxide.

The separation from chromium, molybdenum and tungsten cannot be accomplished in this way, for the chromates, molybdates and tungstates of mercury and lead are also insoluble. To separate these metals, the solution, free from other metals, is evaporated to a small volume and saturated with ammonium chloride. It has already been mentioned that ammonium metavanadate is practically insoluble in a strong solution of ammonium chloride. The sandy precipitate produced, therefore, is filtered off, washed with ammonium chloride solution, and ignited out of contact with the filter-paper, so as to expel the excess of ammonium chloride and ammonia. Great care is needed to prevent loss of vanadium compounds in the form of fine dust. The ammonium metavanadate is converted to vanadic oxide (V_2O_5) as a result of the ignition, and the vanadium is weighed in that form.

On account of the similarity of phosphates and arsenates to vanadates, the estimation of vanadium in the presence of these salts also may present difficulty. It is best to reduce the vanadium to the blue tetravalent state by the action of sulphur dioxide and then to precipitate the phosphorus as phosphomolybdate; the arsenic can be separated as sulphide; and the vanadium can afterwards be re-oxidized, and estimated as usual.

When other metals which form two series of salts are absent (e.g. iron and copper), vanadium can be determined volumetrically. The vanadium is assumed to be first in the vanadic condition; it is made acid and reduced to the hypovanadic condition by passing in sulphur dioxide. Then it is boiled free from sulphur dioxide, and titrated with potassium permanganate. The amount of permanganate needed to reconvert the solution completely to the vanadic condition is a measure of the amount of vanadium present.

Vanadates can also be estimated by titration with ferrous salts, potassium ferricyanide being used as a side-indicator. An electrometric method has also been worked out in which the end-point is detected by the sudden drop in the P.D. at the surface of a platinum electrode immersed in the solution [1]; in this method the side indicator is dispensed with.

Colorimetric methods of estimating vanadium have also been studied and are useful where the quantity present is small; one method depends on the depth of colour obtained when hydrogen peroxide is added to the solution.[2]

TERRESTRIAL OCCURRENCE

Vanadium is one of the rarer elements, but is nevertheless fairly widely distributed. In igneous rocks, it is found—unlike most of the elements—mainly in the basic and ultrabasic varieties, smaller traces being present in the acidic rocks. Appreciable quantities of vanadium occur in certain magnetites, particularly those containing titanium; thus vanadium is a minor constituent of some iron ores.

In addition, where ore deposits of the heavy metals (lead and copper) have been formed in connection with the intrusions, small quantities of minerals containing vanadium are sometimes found along with the commoner minerals; the vanadates of the heavy metals are often present in those portions of the ores which have undergone oxidation. In the mining district of Arizona and New Mexico, the chloride and vanadate of lead,

Vanadinite . . . $3Pb_3(VO_4)_2.PbCl_2$,

occurs in deep red crystals. These crystals, it should be noticed, are isomorphous with that important natural phosphate,

Apatite . . . $3Ca_3(PO_4)_2.CaF_2$.

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[1] G. L. Kelley and J. B. Conant, *J. Amer. Chem. Soc.* **38** (1916), 341.

[2] P. Slawik, *Chem. Zeit.* **34** (1910), 648, describes a method of this kind adapted for the determination of vanadium in steel.

Similarly in Peru, close to the copper-mining districts, an impure sulphide ore of vanadium occurs; this is called

Pattronite [1] . . VS_3 (?)

It occurs along with iron pyrites and closely associated with a poor coal containing much sulphur.[2]

Many other vanadium minerals exist in nature, such as the basic vanadate of lead and copper,

Mottramite . $[Pb, Cu]_3(VO_4)_2.2[Pb, Cu](OH)_2$,

which has been found in Cheshire. A far more important source of vanadium, however, is the vanadate of uranium which has already been discussed as a source of radium, namely,

Carnotite . . $K_2O.2UO_3.V_2O_5.3H_2O$.

It occurs in Colorado and Utah as a canary-yellow impregnation in sandstones and other rocks. Other sandstones in Colorado contain a micaceous mineral, roscoellite, which contains 2–4 per cent. of vanadium.

Small quantities of vanadium exist in other kinds of deposits. Some samples of bauxite contain appreciable amounts of the rare element, which has also been found in numerous clays. It is noteworthy that plants seem to absorb vanadium where it has passed into the soil, and in this way considerable concentration has been brought about. Thus, numerous samples of coal and asphalt found in different parts of the South American Continent (Argentina and Peru) yield, on burning, an ash which contains vanadic oxide; in some cases, the oxide may represent 38 per cent. of the ash.

TECHNOLOGY AND USES

The most important practical source of vanadium is the sulphide ore of Peru (pattronite), which occurs along with coal, sulphur and pyrites. The whole earth around the patronite veins is impregnated with soluble vanadium compounds, and catch-basins are dug out and allowed to fill with vanadium-bearing waters from which the metal can be recovered. The solid ore is also used as a source of vanadium; it may be roasted and fused with soda, yielding sodium vanadate,[3] which can be extracted by leaching. In another process the ore is extracted with sulphuric acid, which dissolves out the vanadium in the tetravalent state.[4] It is subsequently oxidized and precipitated as iron vanadate, or as vanadic acid. It is stated that the Peruvian supplies are beginning to show signs of exhaustion.

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[1] The formula here ascribed to pattronite is attributed to it by Manz. The mineral is extremely impure, and most authorities do not venture to suggest a formula.

[2] W. F. Hillebrand, *Amer. J. Sci.* 24 (1907), 141.

[3] F. L. Hess, *U.S. Geol. Surv., Min. Res.* (1918), I, 816.

[4] W. F. Bleeker, *Met. Chem. Eng.* 9 (1911), 499.

Practically all the vanadium oxide and iron vanadate produced is mixed with fuel (and with iron ore if necessary) and is smelted to give the important alloy **ferro-vanadium,** which is used largely in the manufacture of certain steels. The matter is further discussed in the section on ferro-alloys (Vol. III). The reduction is usually carried out by means of carbon or silicon in the electric furnace. Steel-makers prefer a ferro-vanadium which has only a small carbon-content, and hence silicon is regarded as the better reducing agent.[1] Another method, depending on the reduction of iron vanadate with aluminium, has also proved very valuable.[2]

A great deal of vanadium is produced from the carnotite ores of Colorado, the treatment of which has already been referred to in the section on radium (page 160). It was stated there that most of the vanadium is separated as iron vanadate, which salt can be used for the manufacture of ferro-vanadium.[3]

Experiments to investigate the possibilities of working the vanadate ores of the Arizona ore-field were underaken a few years ago.[4] The vanadium can best be extracted by leaching with sulphuric acid. Another mineral containing vanadium which has been worked from time to time is the mica, roscoelite; this occurs in Colorado.[5]

Another potential source of vanadium is the slag from steel-works like those of Creuzot, in which pig-iron derived from vanadiferous ores is converted to steel by the basic process. The basic slag produced at most steel-works consists largely of calcium phosphate, but at Creuzot the slag contains a considerable quantity of calcium vanadate also.

Uses. Vanadium is nearly always added to steel as ferro-vanadium. The *rôle* of the element is apparently not merely that of a remover of oxygen and nitrogen; it also seems to have a specific effect upon the metal, which will be discussed in connection with the special steels (Vol. III).

Vanadium salts are useful catalysts, and have been employed as oxygen-carriers in organic chemistry, for instance in the manufacture of aniline black. Recently a specially prepared form of vanadium oxide has been advocated for use in the oxidation of sulphur dioxide to sulphur trioxide, for the oxidation of anthracene to anthraquinone and for many other technically important oxidations.[1] The employment of the resinate or linoleate of vanadium as "driers" for oils has also been strongly recommended; the vanadium salts are said to act much more rapidly than the corresponding manganese or lead salts, and the film of dried oil produced is said to be exceptionally smooth and free from wrinkling.[2]

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[1] R. J. Anderson, *Trans. Amer. Electrochem. Soc.* **37** (1920), 277.

[2] B. D. Saklatwalla, *Trans. Amer. Electrochem. Soc.* **37** (1920), 341.

[3] *U.S. Bur. Mines, Bull.* **104** (1918).

[4] J. E. Conley, *Met. Chem. Eng.* **20** (1919), 465, 514.

[5] H. Manz, *Met. u. Erz.* **10** (1913), 370.

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[1] *J. Soc. Chem. Ind.* **40** (1921), 307R.

[2] F. H. Rhodes and K. S. Chen, *J. Ind. Eng. Chem.* **14** (1922), 222.

NIOBIUM

Atomic weight 93·1

Niobium (which is also known as *columbium*) shows a general resemblance to vanadium, and an analogy exists between many of the compounds of the two metals; but the oxides of niobium have only very feebly-developed basic properties, and the soluble salts are almost unknown in the solid state.

The Metal [1]

Niobium is a white lustrous metal; like vanadium, it is hard, and it has an even higher melting-point (1,950° C.). It is less brittle than vanadium, but not so ductile as tantalum.

Niobium has less tendency towards oxidation than vanadium; it keeps its lustre extraordinarily well when exposed to air at ordinary temperatures, and is only slowly attacked even when heated; a yellow oxide skin is first formed, and at higher temperatures the skin becomes thicker and has a blue tint, the colour being in each case due to interference. When niobium is heated in nitrogen at 1,200° C. it forms a nitride. The metal is unattacked both by hot hydrochloric acid, by nitric acid, and even by aqua regia. It is attacked by hydrofluoric acid, the action being hastened by contact with platinum. Niobium is dissolved by fused caustic alkalis. The apparent "nobility" of niobium, like that of tantalum, is evidently due to a protective film. An anodically polarized niobium electrode shows "valve-action." When an electrolytic cell fitted with a niobium anode is filled with a 0·1 per cent. solution of ammonium phosphate, 530 volts must be applied before the current breaks through the anodic film. When the niobium is made the cathode, a very small E.M.F. suffices to send current through the cell.[2]

Laboratory Preparation. Niobium is much more easily reduced to the metallic state than vanadium. It can be obtained by passing hydrogen mixed with the vapour of the pentachloride ($NbCl_5$) through a red-hot tube. It can be produced from the oxides by reduction with carbon or with aluminium; but the product generally contains small amounts of carbon in the one case and of aluminium in the other. The aluminium can be expelled by heating strongly in an electric vacuum furnace, but such a furnace is not often available in an ordinary laboratory. A more suitable reducing agent is, as in the case of vanadium, mischmetall; when a mixture of powdered mischmetall and niobic oxide is heated, a violent action takes place and very moderately pure niobium is produced.

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[1] W. Muthmann, L. Weiss and R. Riedelbauch, *Lieb. Ann.* **355** (1907), 68; W. von Bolton, *Zeitsch. Elektrochem.* **13** (1907), 145.

[2] G. Schulze, *Ann. Phys.* **25** (1908), 775.

Compounds

Three oxides of niobium are known, Nb_2O_5, NbO_2 and NbO. The first two appear to possess weakly basic properties, although no salts of oxy-acids have been obtained in a solid state. The highest oxide (Nb_2O_5), from which all the more stable niobium compounds are derived, has a well developed acidic character. Certain derivatives of a yet higher oxide (Nb_2O_7), itself unknown, can be obtained. No oxide corresponding to vanadous oxide (V_2O_3) has been prepared, but another intermediate oxide (Nb_3O_5) has been described, although its existence cannot be looked upon as certain.

A. Compounds of Pentavalent Niobium (Niobic Compounds).

The **pentoxide**, Nb_2O_5, is formed when the metal or the lower oxides are ignited in air; it is a white infusible substance. The hydrated oxide (*niobic acid*) is obtained when the solution of a niobate is precipitated by sulphuric acid, and comes down as a voluminous precipitate which cannot be freed from adsorbed sulphate by washing; it readily passes into colloidal solution when washed with pure water, and penetrates through the filter-paper. The acid yields anhydrous niobic oxide on ignition. Niobic acid and even the anhydrous oxide (provided the ignition has not been too strong) dissolve in concentrated sulphuric acid. The solution may contain a sulphate, but if it is diluted and boiled, hydrolysis occurs, and the whole of the niobium is precipitated as niobic acid. Niobic acid is scarcely dissolved by hydrochloric acid, but after digestion with the acid, a residue is obtained which, although insoluble in hydrochloric acid, yields a colloidal solution with water. Traces of niobium salts in the residue act no doubt as peptizing agents. The colloidal solution is precipitated by traces of acids and by many neutral salts. The behaviour is, of course, analogous to that of vanadium oxide.

Niobic oxide dissolves quite readily in hydrofluoric acid, and from this solution, as in the case of vanadium, it is possible to obtain crystalline double salts. For instance, by adding potassium or ammonium fluoride to the solution, **double basic fluorides**, such as $NbOF_3.2KF$ and $NbOF_3.2NH_4F$, are deposited in colourless crystals.

A few insoluble niobic salts can be obtained by precipitation. When potassium ferrocyanide is added to the solution of a niobic salt (e.g. a solution of potassium niobate acidified with hydrochloric acid), a red-brown precipitate is produced. Under the same conditions, potassium ferricyanide causes a bright yellow precipitate.

Niobic oxide is soluble in caustic potash solution, potassium niobate being no doubt formed. In order to obtain the **niobates** in a solid state, however, it is best to fuse niobic oxide with the carbonate of sodium or potassium, and then to recrystallize the product from water. A very large number of so-called niobates have been described, but many of them are probably mixtures, mixed crystals or adsorption compounds. It is stated that when a mixture of niobic oxide with two to three parts of potassium carbonate is heated to fusion and then extracted with water, the solution on evaporation yields colourless monoclinic prisms of the composition $4K_2O.3Nb_2O_5.16H_2O$. If the same solution is evaporated with potassium hydroxide, pyramids of the salt $3K_2O.2Nb_2O_5.13H_2O$ are obtained.

B. Compounds of Tetravalent Niobium (Hyponiobic Compounds).

When niobic oxide (Nb_2O_5) is strongly heated in hydrogen, it is reduced to hyponiobic oxide, NbO_2, which is a bluish-black substance. Possibly owing to the high temperature needed for its production, it is not perceptibly dissolved in acids. Salts corresponding to this oxide, however, are probably present in the blue solution obtained by reducing a solution of niobic chloride (i.e. a solution of a niobate acidified with hydrochloric acid) with zinc; the reduction can also be brought about electrolytically, a platinum cathode being conveniently employed, if it is desired to stop the reduction at the tetravalent state. It will be remembered that the corresponding vanadium compounds also show a blue colour in solution.

C. Compounds of Trivalent Niobium (Niobous Compounds).[1]

Further electrolytic reduction with the use of a lead-amalgam cathode gives a brown-black liquid having very strong reducing properties; it yields a brownish precipitate with ammonia, which may contain $Nb(OH)_3$, although this point appears to be undecided.

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[1] A. Stähler, *Ber.* **47** (1914), 841. See also F. Ott, *Zeitsch. Elektrochem.* **18** (1912), 349. These two authorities differ somewhat in their statements.

D. Compounds of Divalent Niobium (Hyponiobous Compounds).

Hyponiobous oxide, NbO, is obtained when potassium niobium basic fluoride ($NbOF_3.2KF$) is heated with sodium or magnesium. It is stated to be white when pure,[1] although, as usually produced, it has a dark colour. No salts corresponding to this oxide are known; when the oxide is dissolved in acids, hydrogen is evolved and the salts of the higher oxides are produced.

E. Highly Oxidized Compounds of Niobium.

As in the case of vanadium, a series of yellow per-salts are known. When a solution of potassium niobate is treated with hydrogen peroxide, a yellow coloration is produced, and by the addition of alcohol, potassium perniobate can be precipitated. By the action of sulphuric acid on the potassium salt, perniobic acid, $HNbO_4.nH_2O$, may be produced as a yellow colloidal solution, which can be purified by dialysis. On evaporation, a precipitate comes down, which, when dried over sulphuric acid, yields a yellow amorphous powder.[2]

F. Miscellaneous Compounds.

Chlorides of Niobium. As has been stated, it is impossible to obtain the chlorides of niobium from aqueous solutions. Two chlorides, however, can be obtained in a dry way. The **pentachloride,** $NbCl_5$, is formed when a current of dry chlorine gas is passed over a mixture of niobic oxide and excess of carbon heated in a hard-glass tube. It is a yellow substance, crystallizing in needles, and melts at 194° C., but is volatile at a lower temperature. If less carbon is used for the preparation, the colourless **oxychloride,** $NbOCl_3$, is obtained in addition to the pentachloride; the separation of the two bodies is brought about by distillation in hydrogen, the oxychloride being the less volatile of the two. When either compound is treated with water, hydrolysis occurs almost at once, niobic acid being precipitated; but in the presence of free hydrochloric acid the solution is more stable. The vapour of the pentachloride has a normal density, corresponding to the formula $NbCl_5$ at moderate temperatures; but, if passed through a red-hot tube, it partially decomposes, depositing the non-volatile **trichloride,** $NbCl_3$, in grey flakes of metallic appearance on the sides of the tube.

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[1] H. E. Roscoe and C. Schorlemmer, "Treatise on Chemistry" (Macmillan), Vol. II.

[2] P. Melikoff and L. Pissarjewsky, *Zeitsch. Anorg. Chem.* **20** (1899), 340.

Niobium nitride. A blackish nitride is formed when the metal is heated in a current of nitrogen.[1] The oxychloride ($NbOCl_3$) reacts with ammonia, and, when heated strongly, the product evolves ammonium chloride, and leaves a black nitride as residue.[2] In the present state of our knowledge, it is probably best not to try and assign formulæ to these products.

Analytical

The solution of a niobate treated with potassium ferrocyanide in the presence of acid gives a reddish-brown precipitate; if treated with tannic acid a precipitate of a reddish chocolate colour appears. Acidified solutions of a niobate become blue when treated with zinc, and yellow when treated with hydrogen peroxide, but several other metals (including vanadium) behave in the same way.[3]

In the separation from other metals advantage is taken of the feebly basic character of niobium. If all the metals (including niobium) in a mixture are present as oxides, the mixture can be fused with sodium bisulphate; most of the metals are converted to soluble salts, and can be leached out by the action of water or dilute hydrochloric acid. On boiling, the hydroxides of niobium, tantalum, tin, tungsten, and certain other metals are precipitated, owing to hydrolysis; but of these tin and tungsten can be converted to soluble complex sulphides by fusion with sulphur and sodium carbonate, and can be separated by lixiviation. Some niobium and tantalum remain in the insoluble residue, with small quantities of certain oxides like iron, which do not readily pass into the form of soluble sulphates; to remove these it may be necessary to repeat the fusion with sodium bisulphate, or to boil the residue with dilute sulphuric acid, before the whole of the iron, etc., is removed; niobium and tantalum are undissolved by the dilute acid.

Similar methods may be applied to the analysis of minerals containing niobium and tantalum, which may be "opened up" by fusion of the finely powdered material with sodium bisulphate. It has been found that if the melt is extracted with tartaric acid—which serves to restrain the hydrolysis—the whole of the niobium and tantalum can be brought into solution; in this way, the separation of these metals from silica can be attained. The separation from zirconia presents a difficult problem, but it has been found that if the mixed oxides of zirconium, niobium and tantalum are fused with potassium carbonate, and leached with hot water, most of the niobium and tantalum pass into solution whilst the zirconia remains undissolved; but it is necessary to repeat the fusion—generally twice—before the whole of the tantalum is rendered soluble.[1]

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[1] W. Muthmann, L. Weiss, R. Riedelbauch, *Lieb. Ann.* **355** (1907), 94.

[2] H. E. Roscoe and C. Schorlemmer, "Treatise on Chemistry" (Macmillan), Vol. II.

[3] Numerous other tests are given by J. Moir, *J. Chem. Met. Min. Soc. S. Africa*, **16** (1916), 189.

The separation of niobium and tantalum from one another is a difficult matter; the processes usually described in the textbooks (e.g. that depending on the difference of solubility of the double potassium fluorides) are tedious and require experience before even moderately good results can be obtained. Probably the quickest method of determining the relative proportions of the two metals in the mixed oxides is to take the specific gravity of the mixture after ignition over a blast lamp in a platinum crucible for an hour (after this period the specific gravity has become quite constant). The result obtained is referred to a curve or table,[2] showing the relation between the specific gravity and composition of mixtures. Since the density of pure tantalum oxide (8·716) is nearly twice that of pure niobium oxide (4·552), this method, carried out with care, yields fairly accurate results.

Recently a method of analytical separation has been described depending on the fact that when the ignited oxides of niobium and tantalum are boiled with a mixture of selenium oxychloride and sulphuric acid, the whole of the niobium can finally be brought into solution, whilst tantalum oxide remains undissolved.[3]

TERRESTRIAL OCCURRENCE AND TECHNOLOGY

Since niobium occurs along with tantalum in nature, the discussion of its geochemistry can be deferred until the section on tantalum. Except in so far as it may be a constituent of impure tantalum, niobium has little industrial importance. A certain quantity of the mineral columbite has been mined and marketed in America, but mainly for experimental purposes.[4]

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[1] W. R. Schoeller and A. R. Powell, *Trans. Chem. Soc.* **119** (1921), 1927. Compare E. S. Simpson, *Chem. News*, 99 (1909), 243.

[2] Given by H. W. Foot and R. W. Langley, *Amer. J. Sci.* **30** (1910), 393, 401.

[3] H. B. Merrill, *J. Amer. Chem. Soc.* **43** (1921), 2378.

[4] F. L. Hess, *U.S. Geol. Surv., Min. Res.* (1918), I, 807.

TANTALUM

Atomic weight 181·5

The Metal[1]

Tantalum is, like niobium, a lustrous metal, melting at an exceedingly high temperature (between 2,250° and 2,300° C.), far above the melting-points of iron and platinum. In colour, tantalum is rather whiter than niobium; it is a heavy metal, the specific gravity being 16·6. The metal crystallizes in the cubic system, the atoms being arrayed on a centred cube space-lattice.[2] Pure tantalum is very ductile and malleable, and tantalum wire is extremely strong. The pure, gas-free metal can be rendered extremely hard by mechanical work without becoming brittle. Tantalum containing hydrogen, nitrogen, or carbon, however, is apt to be distinctly brittle.

When heated in air, tantalum oxidizes superficially becoming, like most metals, first yellow and then blue; but, to a large extent, the oxide-film protects the metal from further oxidation. In the fine state of division, however, tantalum is rapidly burnt to oxide. Tantalum is dissolved by hydrofluoric acid, especially when placed in contact with platinum or carbon, materials which can function as the cathodic element of the corrosion couple. None of the other acids, however, attack tantalum; this is no doubt connected with the fact that the oxide of tantalum has very weak basic properties, and is practically undissolved by any acids other than hydrofluoric. Thus, in effect, tantalum behaves as though it were one of the most noble of metals, and is frequently described as being similar in chemical behaviour to platinum.

A tantalum electrode immersed in the solution of any salt other than a fluoride shows valve-action, similar to that displayed by niobium and aluminium.[3] Anodically polarized tantalum becomes covered with a bluish film of oxide, but the true seat of the valve-action is probably the layer of oxygen gas which is produced within the pores of the oxide film. The gas layer allows electrons to pass from metal to solution, but not in the opposite direction. In a very dilute solution of sodium carbonate, an E.M.F. of about 650 volts must be applied to an electrolytic cell fitted with a tantalum anode, before any considerable current can be forced through.

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[1] A. Siemens, *Chem. News*, **100** (1909), 223.

[2] A. W. Hull, *Phys. Rev.* **17** (1921), 571.

[3] G. Schulze, *Ann. Phys.* **23** (1907), 226.

In fluoride solutions, valve-action is practically absent. Consequently, attempts have been made to measure the electrode potential of tantalum in fluoride solutions. The value depends greatly on the previous treatment of the metal, cathodically polarized tantalum (containing hydrogen) having a comparatively low potential, whilst anodically polarized ("passive") tantalum has a value abnormally high (positive). The value of the potential at the electrode

$$\mathrm{Ta}\;\Big|\;\begin{matrix}0{\cdot}006\ \mathrm{Mol.}\\ \mathrm{TaF_5}\end{matrix}$$

has been measured and found to be

$$+\,0{\cdot}165\ \text{volts},$$[1]

when tantalum is in the most active condition obtainable. It seems, however, unlikely that this represents the true equilibrium conditions of the change

$$\mathrm{Ta} \rightleftharpoons \mathrm{Ta}^{\cdot\cdot\cdot\cdot\cdot} + 5e$$

since, if that were the case, tantalum should be as easy to deposit from aqueous solution as tin. It is probable, therefore, that tantalum is covered with a partially protective film even in fluoride solutions, and is thus never met with in the completely active condition. Another difficulty confronting those who would endeavour to assign a place for tantalum in the Potential Series is the fact that we do not know the ion-concentration of a tantalum fluoride solution.

Laboratory Preparation. Tantalum can be obtained from its compounds in various ways. Reduction of the oxide with carbon yields a product containing carbon, whilst reduction of one of the compounds (e.g. a complex fluoride) with potassium rarely yields the metal in a pure state. The product becomes purer if heated *in vacuo* at a very high temperature as many of the impurities volatilize away. A suitable method for obtaining pure tantalum, based upon the reduction of the pentoxide with mischmetall, has been described, and is generally similar to the method used for vanadium and niobium; but the reaction is slower, and the metal obtained is often less thoroughly fused, and is apt to be mixed with oxide.[2] Pure tantalum can be made, however, by the electrolysis of fused potassium tantalifluoride (K_2TaF_7), the product being subsequently heated electrically *in vacuo* to volatilize any traces of oxide that may be present.[3]

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[1] G. von Hevesy and R. E. Slade, *Zeitsch. Elektrochem.* **18** (1912), 1001.

[2] W. Muthmann, L. Weiss and R. Riedelbauch, *Lieb. Ann.* **355** (1907), 65.

[3] W. von Bolton, *Zeitsch. Angew. Chem.* **19** (1906), 1537.

Compounds

As in the case of niobium, all the stable compounds of tantalum correspond to the pentoxide, Ta_2O_5. Its basic qualities are, however, even more feebly developed than those of niobium pentoxide and vanadium pentoxide. There is a lower oxide, TaO_2, but few derivatives are known. The oxide, TaO, corresponding to NbO, has not been prepared, although a chloride, $TaCl_2$, is known. Derivatives of a higher state of oxidation than Ta_2O_5 have been isolated.

A. Compounds of Pentavalent Tantalum.

The **pentoxide,** Ta_2O_5, is obtained when the metal or the lower oxide is heated in oxygen; it is a white infusible powder. The hydrate, known as **tantalic acid,** $HTaO_3$, is formed when the chloride ($TaCl_5$) is hydrolysed by the addition of water, and is a gelatinous precipitate. When freshly precipitated it dissolves easily enough in hydrofluoric acid, but like other gelatinous hydroxides it tends to " age " and lose its reactivity. The solution in hydrofluoric acid contains **tantalum fluoride** (TaF_5), but it is not very easy to isolate this salt from the solution; by evaporation *in vacuo* it is possible to obtain it in colourless crystals, mixed with a basic fluoride. When, however, alkali-metal fluorides are added to the solution, complex fluorides can be easily obtained by crystallization. By the addition of potassium fluoride to a hot solution of tantalum oxide in hydrofluoric acid, for instance, **potassium tantalifluoride** ($2KF.TaF_5$ or K_2TaF_7) separates in needle-shaped crystals. It is somewhat sparingly soluble in cold water, but dissolves much more readily in hot water; it appears to ionize as a complex salt, $K_2[TaF_7]$. Many other tantalifluorides are known.

The insoluble ferrocyanide of tantalum is obtained by treating a tantalate solution with potassium ferrocyanide, and is a yellow precipitate.

The acidic character of tantalum pentoxide is less feeble than the basic character. Tantalic acid is soluble in solutions of caustic alkalis, **tantalates** being formed; the same substances are produced when the anhydrous oxide is treated with a fused alkali. The soluble tantalates obtained by the crystallization of a solution of tantalic oxide in alkaline hydroxide have such compositions as $Na_8Ta_6O_{19}.25H_2O$ and $K_8Ta_6O_{19}.16H_2O$; they are colourless compounds. From their solutions insoluble tantalates of analogous composition, such as magnesium tantalate, $Mg_4Ta_6O_{19}$, are obtained.

B. Compounds of Tetravalent Tantalum.

Hypotantalic oxide, TaO, is formed when the pentoxide is heated with magnesium. It is a grey substance, unattacked by acids. No salts are known, but the corresponding **sulphide**, TaS_2, is obtained by heating the pentoxide in hydrogen gas loaded with the vapour of carbon disulphide. The sulphide is a grey or yellowish substance, undissolved by hydrochloric acid.

C. Highly Oxidized Compounds of Tantalum.[1]

When a potassium tantalate solution is treated with hydrogen peroxide and then with alcohol, a white precipitate of **potassium pertantalate**, $2K_3TaO_8.H_2O$, is thrown down. By the action of dilute sulphuric acid upon the potassium salt, **pertantalic acid**, which has the formula $HTaO_4$, is obtained; this is also a white substance.

D. Miscellaneous Compounds.

Chlorides of Tantalum. The **pentachloride** of tantalum, $TaCl_5$, is formed in exactly the same way as that of niobium, namely by passing chlorine over a heated mixture of tantalum pentoxide and carbon. It closely resembles the niobium compound, forming pale yellow crystalline needles, which melt at 211° C., and are quite volatile below that temperature. It is at once hydrolysed by water, tantalic acid being produced.

When heated with aluminium in the presence of aluminium chloride, the pentachloride suffers reduction to a mixture of lower chlorides. If the product is heated at 350–400° C., so as to drive off the aluminium chloride, the residue consists mainly of the **trichloride**, $TaCl_3$, which is green, and dissolves in water, yielding deep green solution. If the heating is conducted at a higher temperature (510° C.) tantalum pentachloride is driven off, and the residue consists of a mixture of the trichloride and a black-green **dichloride**, $TaCl_2$, which is insoluble in water.[2]

Nitrides and "Hydrides." Like niobium chloride, tantalum chloride absorbs ammonia, and, if the product is heated gently in ammonia gas, a yellow nitride is obtained, stated to possess the formula Ta[illegible]N_5. If, however, the heating is conducted at a higher temperature, a black nitride containing less nitrogen (possibly TaN) is obtained.[3] Like most nitrides, it has a metallic lustre, and in this case the pseudo-metallic character is further emphasized by the fact that it is a good conductor of electricity. Tantalum heated in nitrogen also takes up the gas, forming a black nitride.[4] The formulæ given must be accepted with caution; the work requires to be revised in the light of recent research on the combination, dissolution and absorption of gases by other metals, notably palladium.

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[1] P. Melikoff and L. Pissarjewsky, *Zeitsch. Anorg. Chem.* **20** (1899), 344.

[2] O. Ruff and F. Thomas, *Ber.* **55** (1922), 1466.

[3] H. E. Roscoe and C. Schorlemmer, "Treatise on Chemistry", (Macmillan), Vol. II.

[4] W. Muthmann, L. Weiss and R. Riedelbauch, *Lieb. Ann.* **355** (1907), 94.

Even greater caution should be observed whilst considering statements regarding the existence of hydrides of tantalum. Tantalum takes up large quantities of hydrogen when exposed to the gas, but the amount absorbed varies continuously both with temperature and pressure.[1] At constant temperature, the quantity of hydrogen taken up by tantalum is proportional to the square root of the pressure. This would seem to indicate that the hydrogen enters the tantalum as single atoms, not as molecules; there is no conclusive evidence of the existence of any definite hydride. The general character of the absorption is similar to that displayed by palladium. A tantalum cathode employed in an acid solution also takes up hydrogen, the metal becoming brittle and the potential being altered in the negative direction.[2]

Analytical

An acidified solution of a tantalate gives a yellow precipitate with potassium ferrocyanide, and also a yellow precipitate with tannic acid. No blue coloration is produced by the action of zinc, and no yellow coloration by the addition of hydrogen peroxide; in this way, tantalum can be distinguished from niobium.

The separation of tantalum and niobium from other metals, and the estimation of the two metals in a mixture, was discussed in the section of niobium (p. 290).

TERRESTRIAL OCCURRENCE OF NIOBIUM AND TANTALUM

Niobium and tantalum are found together in nature almost always as mixed crystals of niobates and tantalates; since the salts are isomorphous, the atoms of the two metals may be present in variable proportions; they clearly fulfil the same *rôle* in the crystal-architecture. The elements, unlike vanadium, have for the most part, become concentrated in the acidic portions of igneous rocks, and are found principally in, or close to, pegmatites. It seems likely that the compounds of tantalum and niobium may actually have been given off by the igneous mass in the vaporous condition; for columbite is commonly found associated with compounds of tin and lithium, metals which are known to have arrived at their present condition by pneumatolytic agency. The impure niobate-tantalate of iron, usually containing manganese and other metals, is known as

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[1] A. Sieverts and E. Bergner, *Ber.* **44** (1911), 2394.

[2] G. Oesterheld, *Zeitsch. Elektrochem.* **19** (1913), 585.

	Columbite .	$Fe(NbO_3)_2$
or		
	Tantalite .	$Fe(TaO_3)_2$,

according as niobium or tantalum predominates. Most specimens, however, contain both elements, and, since manganese often replaces the iron, the general formula may be written

$$(Fe,Mn)((Nb,Ta)O_3)_2.$$

Gigantic masses of columbite are found in the tin-ores of the Black Hills, South Dakota, along with equally huge crystals of the lithium mineral, spodumene. Columbite and tantalite crystallize in the rhombic system.

Many of the ores of the rare-earth metals which have already been described are also niobates and tantalates. For instance, **samarskite** is a niobate-tantalate of cerium, yttrium and other rare metals, as well as of iron and calcium, whilst **euxenite** is a niobate-titanate of cerium, yttrium, erbium and other rare metals, and is often comparatively free from tantalum.

TECHNOLOGY AND USES OF TANTALUM

When electric lamps with metallic filaments were first introduced, two metals were considered suitable, namely tungsten and tantalum. The former would withstand a higher temperature without melting or volatilizing, and seemed, therefore, likely to prove more efficient; but tantalum had the great advantage of being ductile, and therefore capable of being drawn out into wire by direct means. Consequently, a considerable tantalum industry sprang up, especially in Germany,[1] the principal source of the metal being Scandinavian tantalite; tantalite is superior to other tantalum minerals as it is often nearly free from niobium. The manufacture of tantalum was afterwards conducted in this country.[2] However, the discovery of a process of rendering tungsten ductile has nullified the special advantage of tantalum as a material for electric filaments.

No doubt for this reason, efforts have been made by those interested in the tantalum industry to find new uses for the metal, and it has become of great service for many purposes for which the more precious material, platinum, was at one time thought necessary. For dental instruments, tantalum is said to have proved very satisfactory, being hard, uncorrodible and easily sterilized.[1] Weights made of tantalum (instead of platinum-iridium) have received the official approval of the International Atomic Weight Committee for scientific use, and may be regarded, therefore, as entirely reliable.[2] It has also been proposed to use tantalum as an electrode material,[3] but it appears to be scarcely adapted for this purpose. As an anode material, it is admitted by all to be unsuited, on account of valve-action; even when employed as a cathode, it is liable to become brittle, through taking up hydrogen, if the current density becomes unduly high.

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[1] W. von Bolton, *Zeitsch. Angew. Chem.* **19** (1906), 1537.

[2] S. J. Johnstone, *J. Soc. Chem. Ind.* **35** (1916), 812.

Little information is available regarding the method now used in working up the ores of tantalum. It is understood that the mineral is ground and fused with potassium bisulphate and the product leached with water. The tantalum oxide, which either remains undissolved or is reprecipitated on boiling, is purified somewhat by boiling with hydrochloric acid, which dissolves away most of the metals with strongly basic properties. The tantalum oxide is then dissolved in hot hydrofluoric acid, and potassium fluoride is added; the solution deposits the rather sparingly soluble salt, potassium tantalifluoride (K_2TaF_7). By fractional crystallization, this salt can be purified. When sufficiently pure, it is fused and electrolysed—or treated with potassium—to give metallic tantalum. The metal is afterwards heated *in vacuo*, so as to expel the last trace of impurities; this gives a ductile product. The tantalum obtained by reduction of the oxide with carbon contains carbide, and is less satisfactory.

The electrical refining of crude tantalum is perfectly possible, if a bath of fused potassium tantalifluoride is employed. The crude metal is used as anode; tantalum passes into the bath at the anode, and the pure metal is deposited on the cathode.[4]

In addition to the uses referred to above, tantalum has been employed as a constituent of certain special steels.

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[1] E. Cahen, *Discovery*, 1 (1920), 143.

[2] See *Nature*, 87 (1911), 251.

[3] Cf. Brunck, *Chem. Zeit.* **36** (1912), 1232; **38** (1914), 565.

[4] *Met. Chem. Eng.* 8 (1910), 150.

GROUP VIA

	Atomic Weight.
Chromium	52·0
Molybdenum	96·0
Tungsten	184·0
Uranium	238·2

The metals of Group VIA differ from those of Group VA in being far less malleable; like the metals of the previous group, they are extremely infusible, tungsten having a higher melting-point than any other metal.

All the elements of the group have a maximum valency of six, and form stable oxides of the type MO_3; but there are also, in every case, stable compounds corresponding to lower valencies. As usual, the higher oxide tends to have an acidic character, and the lower oxides a comparatively basic character. A certain analogy exists between the metals of Group VIA and the elements of Group VIB (sulphur, selenium and tellurium). The chromates, for instance, have formulæ analogous to the sulphates, and are often isomorphous with them; there is a connection between the solubilities of the two classes of salts.

As in most cases of elements of variable valency, the compounds are often coloured, and the colour is more pronounced in chromium than in the elements of higher atomic weight; this is interesting in view of the fact that chromium falls in the Periodic Table by the side of vanadium, which shows such a remarkable range of coloured compounds.

The metals differ from those of the previous group in electrochemical properties; an electrode composed of a metal of Group VIA does not, as a rule, show valve action, but easily becomes passive. Substances which have a solvent action on the oxides tend to restore activity. It is difficult to assign a characteristic electrode potential to any of the metals, because the values obtained depend on the previous history of the electrode. This is shown by the table below,[1] which indicates how widely the value of the potential towards a normal solution of potassium chloride varies after different kinds of treatment; it should be added that the values refer to samples of metal which are not absolutely pure. In the case of chromium, the value given for the freshly-ground surface probably shows the approximate position of the metal in the Potential Series, and the more negative value obtained by cathodic treatment is due to hydrogen. In the case of the other metals, however, this is not necessarily true.

	Rendered active (by cathodic treatment in cooled alkaline solution).	**Fresh Surface** (ground with emery).	**Rendered passive** (by immersion in chromic acid).
Chromium . .	− 0·63 volts	− 0·43 volts	+ 1·19 volts
Molybdenum .	− 0·74 volts	− 0·31 volts	+ 0·66 volts
Tungsten . .	−0·62 volts	− 0·27 volts	+ 0·88 volts

It should be understood that these numbers do not represent the normal electrode potentials of the metals in question, being obtained with an electrode immersed in *potassium chloride* solutions. The results of the attempts which have been made by later workers to obtain the true “ normal electrode potentials ” of the elements of Group VIA are open to more than one interpretation, and will not be considered here.

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[1] From numbers given by W. Muthmann and F. Fraunberger, *Sitzungsber. Bayer. Akad.* **34** (1904), 201. (Converted to hydrogen scale.) Compare also A. H. W. Aten, *Proc. Amst. Acad.* **20** (1918), 812.

CHROMIUM

Atomic weight 52·0

The Metal

In physical properties metallic chromium is not unlike the lower elements of the last group, being a hard grey substance, assuming a metallic lustre when polished, and having a very high melting-point (between 1,520° and 1,530° C.). It has a specific gravity of 6·92, similar to that of zinc. The hardness of chromium is greatly increased by the presence of small quantities of carbon.

Compact chromium is not appreciably affected by exposure to the atmosphere. It oxidizes only when heated to a very high temperature. As usual, the apparent stability of the compact metal in air is to be attributed mainly to the presence of a closely adherent oxide-film, for chromium-amalgam is readily oxidized by the atmosphere, and the finely divided chromium obtained from the amalgam by driving off the mercury takes fire spontaneously when exposed to air.

Chromium dissolves in dilute sulphuric or hydrochloric acid on warming, hydrogen being evolved, whilst blue chromous salts ($CrCl_2$ or $CrSO_4$) are formed in the solution. But it becomes passive when immersed in concentrated nitric acid. Even those reagents which have a solvent action upon chromium often show "periodicity," the chromium being insoluble one minute, and soluble the next. This behaviour is commonly met with in metals which tend to become passive.

The passivity of chromium, however, is best understood by studying the behaviour of a chromium anode.[1] When chromium is made the anode of a cell containing hydrochloric acid, it dissolves almost quantitatively, passing into the solution as chromous ions ($Cr^{\cdot\cdot}$) which give a blue colour to the solution round the anode. If it is made the anode in a sulphate or nitrate solution, the same sort of dissolution may occur (at least for a time), if the current density is low. If, however, the E.M.F. applied to the cell is increased, the chromium becomes passive and ceases to dissolve as a chromous salt; accordingly the current dies away. If finally the E.M.F. applied to the cell is increased still further, the chromium commences to dissolve once more, not, however, as a blue chromous salt, but as yellow chromic acid (CrO$_3$). The formation of this endothermic, highly oxidized substance needs a high anodic potential (at least + 1·1 volts). If the solution contains an iodide, it will be impossible to reach so positive a value, since iodine ions are discharged at about + 0·6 volts, and consequently the addition of an iodide to the bath prevents the dissolution of chromium as yellow chromic acid. (For further discussion of "passivity" see Vol. I, Chapter XII).

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[1] W. Hittorf, *Zeitsch. Phys. Chem.* **25** (1898), 729; **30** (1899), 481; C. W. Bennett and W. S. Burnham, *Trans. Amer. Electrochem. Soc.* **29** (1916), 252; A. H. W. Aten, *Proc. Amst. Acad.* **20** (1918), 1119.

Passive chromium exhibits a potential similar to that of platinum, although active chromium falls between zinc and cadmium in the Potential Series.

Laboratory Preparation. Chromium differs from most of the metals so far considered in being capable of electrolytic deposition from an aqueous solution. If a solution of chromic chloride, CrCl$_3$, containing 10 per cent. of chromium, is electrolysed at a fairly low cathodic current density (0·9 amps. per sq. dm.), only an oxide of chromium is deposited on the cathode. But if the current density is raised to 9 amps. per sq. dm. then the deposition of metallic chromium may begin. The high current density is needed to ensure that the cathodic potential is sufficiently negative for the deposition of the metal. The deposition is, however, not efficient, and the metal obtained is usually far from pure. At a high concentration of chromic chloride, the deposit contains chromous chloride (CrCl$_2$), whereas at lower concentrations it is apt to be contaminated with oxide.[1] Chromium amalgam is, however, more readily produced, being formed whenever a chromium salt solution is electrolysed with a mercury cathode. When this amalgam is distilled at 350° C. in hydrogen, chromium is left behind in a finely-divided form; in fact, if distilled at a rather higher temperature, the residue is pyrophoric.[2]

Electrolysis is not, however, the easiest method of obtaining metallic chromium. The oxide may be reduced to the metallic state by heating with carbon or with aluminium, or with dry hydrogen under pressure. In the first case the product contains a great deal of carbide, which has a considerable effect in modifying the properties of the metal. Reduction with aluminium ("thermite" process) is capable of giving much purer chromium, and is the process commonly employed.[3] A dry mixture of aluminium powder and green chromic oxide is prepared and placed in a magnesia crucible. A pill consisting of aluminium powder and barium peroxide is made ; a piece of magnesium is stuck into it, and the pill is embedded in the mixture. The magnesium is lighted, and the aluminium of the pill reacts with the barium peroxide, producing a temperature high enough to start the reaction in the body of the mixture. The change

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[1] M. Le Blanc, "Production of Chromium and Compounds by the Aid of the Electric Current." Translation by J. W. Richards (Chemical Publishing Co.). See also S. J. Sargent, *Trans. Amer. Electrochem. Soc.* **37** (1920), 479. Also compare E. Liebreich, *Zeitsch. Elektrochem.* **27** (1921), 94.

[2] H. Moissan, "Traité de Chimie Minérale" (Masson).

[3] H. Goldschmidt and C. Vautin, *J. Soc. Chem. Ind.* **1[illegible]** (1898), 543.

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3$$

occurs so quickly and causes the evolution of so much heat that the chromium produced becomes molten, and collects at the bottom of the crucible. After cooling the mass may be broken up, and a button of solid chromium will be found at the bottom.

Another method which, it is claimed, yields chromium in a state of great purity consists in heating the green oxide in dry hydrogen at a high pressure (130 atmospheres) in a magnesia crucible wound externally with tungsten wire, which is itself surrounded by heat-insulating material.[1] By passing a heavy current through the wire, a temperature of over 2,000° C. can be reached. It is best to introduce a little sodium into the cooler part of the furnace to absorb water vapour. The equilibrium of the balanced reaction,

$$CrO + H_2 \rightleftharpoons Cr + H_2O,$$

is naturally shifted in the sense desired by increasing the pressure of hydrogen, and by decreasing the pressure of water vapour. At ordinary pressures, hydrogen does not bring about appreciable reduction of the oxide of chromium.

Compounds

Three important oxides of chromium are known, CrO, Cr_2O_3 and CrO_3, each of which forms a definite class of compounds. The two lower oxides (CrO and Cr_2O_3) are basic ; the highest (CrO_3) is acidic. The oxide, Cr_2O_3, also seems to possess feeble acidic properties. Certain intermediate oxides such as CrO_2 can be obtained, but no derivatives have been prepared. Many compounds of chromium in a higher state of oxidation than CrO_3 are known.

A. Compounds of Divalent Chromium (Chromous Compounds).

Chromous oxide, CrO, is formed when chromium amalgam is exposed to the air. It is most conveniently prepared by treating chromium amalgam with dilute nitric acid.[2] On gentle warming, the mercury dissolves and the chromous oxide remains as a black powder. The corresponding **hydroxide,** $Cr(OH)_2$, is obtained as a brown-yellow precipitate when a chromous salt solution is precipitated with ammonia. Both anhydrous oxide and hydroxide are readily oxidized by the air to chromic oxide.

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[1] E. Newbery and J. N. Pring, *Proc. Roy. Soc.* 92 [A] (1916), 276.

[2] T. Dieckmann and O. Hanf, *Zeitsch. Anorg. Chem.* 86 (1914), 301.

Chromous salts are not obtained when chromous oxide dissolves in acids, since—in so far as dissolution occurs at all—hydrogen is evolved and chromic salts are formed. In some cases chromous salts are produced when metallic chromium reacts with a non-oxidizing acid (e.g. dilute sulphuric acid), but they are more conveniently prepared by reduction of one of the higher compounds of chromium, for instance by treating a chromic salt with zinc. In many cases, however, it is better to conduct the reduction electrolytically,[1] a lead cathode being employed; the solution should be covered over with a layer of light petroleum to prevent reoxidation of the chromous salts by the air. The chromous salts have blue solutions with very strong oxidizing properties; they actually evolve hydrogen when warmed or when treated with acids. They reduce acetylene gas (C_2H_2) to ethylene (C_2H_4).

The anhydrous **chloride,** $CrCl_2$, is formed by passing dry hydrogen chloride gas over metallic chromium heated in a tube. It is a colourless compound. If required in solution only, it is more readily obtained by the reduction of potassium dichromate ($K_2Cr_2O_7$) with zinc in the presence of hydrochloric acid. When reduction is complete the solution is blue, but readily absorbs oxygen from the air, becoming green owing to the formation of chromic salts.

The insoluble **chromous acetate,** $Cr(COO.CH_3)_2$, is obtained by precipitation of chromous chloride solution with sodium acetate; it is a red precipitate, soluble in acids and affords on that account a means for obtaining various soluble chromous salts. For instance, **chromous sulphate,** $CrSO_4.7H_2O$, can be isolated in blue monoclinic crystals, isomorphous with zinc sulphate and ferrous sulphate, from the solution of chromous acetate in sulphuric acid. The preparation of all chromous salts is, however, made difficult by the fact that they are so easily oxidized. Several, like the **formate** and **malonate,** are red in the crystalline state.

B. Compounds of Trivalent Chromium (Chromic Compounds).

Chromic oxide, Cr_2O_3, is obtained when any of the other oxides are ignited in the presence of air at a high temperature. It is most easily prepared in the anhydrous condition by warming solid ammonium dichromate in a hard-glass flask. The change,

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[1] W. Traube and A. Goodson, *Ber.* 49 (1916), 1679, 1692.

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O,$$

when once started, is rather violent, light and heat being given out; after the reaction, chromic oxide is left behind as a green powder.

The **hydroxide** is obtained by precipitating the solution of a chromic salt with ammonia. It is a gelatinous precipitate which undergoes the phenomenon of "ageing," already noted in the hydroxides of beryllium and aluminium. When freshly precipitated, it is readily dissolved by acids or peptized by alkalis; but if stored for some time it becomes less reactive. The ageing is perceptible after a few minutes, but continues for some months. It appears to be due to a decrease in the surface area of the product, which becomes denser and more compact. If the precipitate is heated rather rapidly to about 540° C., the agglomeration (or passage to the denser form) takes place rapidly and quite suddenly, with so great an evolution of heat that the mass becomes incandescent, the temperature rising spontaneously through another 50–100°.[1] This evolution of heat is a sign of the sudden drop in the surface energy of the mass as the surface area becomes so greatly reduced.

Freshly precipitated chromic hydroxide readily passes into colloidal solution, being peptized either by alkalis or by water containing a chromic salt. In both cases, the hydroxide can be separated from the colloidal solution by means of ultra-filtration.[2] Nevertheless, the liquid obtained by shaking chromium hydroxide with a solution of sodium hydroxide is thought by some chemists to contain traces of "**chromites**" in true solution, since the liquid is oxidized by the air yielding a chromate, and the amount of chromate formed increases with the concentration of the alkali employed.[3] The arguments for and against the existence of soluble chromites of definite composition cannot be discussed further, but it may be stated that the evidence adduced on either side is far from conclusive. It is interesting to note, however, that the insoluble chromites of the heavy metals are well-known bodies. Chromite of iron, for instance, occurs in nature.

Chromic salts are formed when chromic oxide is dissolved by acids, or when a dichromate is reduced by a mild reducing agent, e.g. sulphur dioxide. Two classes of chromic salts exist, both being compounds in the same state of oxidation; the most obvious difference between them lies in the colour of the solutions. In the one class, the salts are blue or dark purple, having *violet* solutions; in the other class both salts and solutions are *green*. If a solution of a chromic salt is kept for some time, an equilibrium between the violet and green salt is set up, so that the solution comes to contain both varieties:—

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[1] L. Wöhler, *Koll. Zeitsch.* **11** (1912), 241; H. B. Weiser, *J. Phys. Chem.* **26** (1922), 401.

[2] C. F. Nagel, *J. Phys. Chem.* **19** (1915), 569; W. D. Bancroft, *Trans. Amer. Electrochem. Soc.* 28 (1915), 351.

[3] J. K. Wood and V. K. Black, *Trans. Chem. Soc.* 109 (1916), 164. Compare H. B. Weiser, *J. Phys. Chem.* 26 (1922), 423, 428.

$$\text{Violet salt} \rightleftharpoons \text{Green salt}.$$

The equilibrium proportions of the violet and green salts vary both with the total concentration and the temperature, the proportion of green being greater in concentrated solutions than in dilute. In moderately strong solutions of most of the salts, when a state of equilibrium is reached, the violet salt predominates at low temperatures and the green variety at high temperatures. Thus, generally speaking, a violet solution, when heated, turns green, and the green solution, when cooled, returns to the violet colour. The rate at which equilibrium is set up, however, varies in different cases. Where a solution of the chloride, nitrate or acetate has been rendered green by warming to 95° C., and then cooled, the return of the violet colour is fairly rapid. In the case of the sulphate, however, it may take some weeks.[1] Furthermore, the velocity of change varies greatly with the temperature. If a green solution of chromic bromide is cooled quickly, and is kept at room temperatures, the change to violet requires some hours; if, however, it is warmed somewhat, the change is much more rapid, although—owing to the shifting of equilibrium—it is less complete, the final product having a blue, rather than a violet tint.[2]

In practically every case the violet salt is less soluble than the corresponding green salt, and it is therefore easier to isolate the violet salts in the crystalline state. Attempts to prepare the green salts by evaporation of the green solutions, often lead to hydrolysis, and a basic salt—or sometimes a gummy colloidal mass containing the hydroxide—is produced. It is wrong to draw the conclusion, however, that the green colour is necessarily due to the presence of basic salts. As a matter of fact, in many cases where definite green salts have been obtained by crystallization, they are found to have the normal composition; for instance, the rhombic green chloride ($CrCl_3.6H_2O$) has the same composition as the monoclinic violet chloride ($CrCl_3.6H_2O$). Actually the addition of an acid to a solution often shifts the equilibrium so as to favour the production of the green salt,[1] which would not be the case if the green colour were due to a basic substance.

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[1] W. R. Whitney, *Zeitsch. Phys. Chem.* **20** (1896), 40.

[2] A. Recoura, *Comptes Rend.* **110** (1890), 1029.

It has long been known that the green solutions have an electrical conductivity different from that of violet solutions of equal concentration, and advantage has been taken of this circumstance to follow the variation in the proportions of the two salts during the process of attaining equilibrium. It has also been known for some time that, in a solution of a green salt, only a fraction of the acid radicle appears to be in reactive condition. Thus, in the case of the chlorides, the whole of the chlorine in a violet solution is precipitated by silver nitrate in the presence of nitric acid, whilst, in the green salt, only one-third is precipitated by the same reagent.

The case of the sulphates is similar; by heating the violet sulphate, $Cr_2(SO_4)_3.18H_2O$, at 90° C., a green sulphate, $Cr_2(SO_4)_3.8H_2O$, is obtained which shows none of the reactions of a sulphate, yielding no precipitate with barium chloride at ordinary temperatures.[2] But after standing for half an hour it undergoes a change, and the product then reacts with barium chloride.

Other green sulphates[3] have been described, which react with barium chloride, part at least of the $(SO_4)''$ being precipitated as barium sulphate. Two of these appear to exist in small amounts in a dilute solution of the violet sulphate which has been kept for a long time so as to arrive at a state of equilibrium. If alcohol is added to such a solution, the ordinary violet salt is precipitated, and there remains in solution a green salt having one-third of its $(SO_4)''$ in a state capable of precipitation by barium chloride. If, however, the "aged" solution of the violet sulphate is first concentrated and then treated with alcohol, the precipitate consists of a lilac-grey salt having approximately two-thirds of its $(SO_4)''$ "precipitatable" by barium chloride. This lilac-grey salt quickly undergoes further changes. Recoura regards it as a double salt formed by combination of one molecule of green sulphate and two molecules of violet sulphate.[4]

It has been shown that in some cases the green and violet salts, when precipitated with alkali, yield green and blue-violet hydroxides respectively. Nevertheless, cases are known where a solution containing more green salt than violet yields a violet hydroxide with ammonia; in view of the relatively small solubility of violet compounds (a generalization which presumably extends to the hydroxide) this is not especially surprising. Other insoluble salts likewise exist in the two forms; thus a violet hydrated phosphate has been obtained by precipitation from cold solutions, and a green hydrated phosphate from hot solutions. The latter gives on gentle heating a black anhydrous phosphate ($CrPO_4$), which yields green basic salts on strong heating.[1]

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[1] J. Olie, *Zeitsch. Anorg. Chem.* **51** (1906), 47.

[2] A. Recoura, *Ann. Chim. Phys.* **4** (1895), 505.

[3] See also A. Colson, *Comptes Rend.* **140** (1905), —.

[4] A. Recoura, *Comptes Rend.* **169** (1919), 1163; **170** (1920), 1494.

The existence and reactions of the various salts is to some extent accounted for on Werner's assumption of a stable "group of six" around each chromium atom, no member of which "group of six" is capable of ionization.[2] According to this theory, we can write the two chlorides,

$$[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3} \qquad \text{Violet Chloride}$$

$$\text{and } \left[\mathrm{Cr}^{(\mathrm{H_2O})_4}_{\mathrm{Cl_2}}\right]\mathrm{Cl.2H_2O} \qquad \text{Green Chloride}$$

thus explaining why only one-third of the chloride of the green salt can be separated by means of silver nitrate. The fact that the green salt loses two of its molecules of water of crystallization when kept over sulphuric acid *in vacuo* adds support to the formulæ just proposed.

In the case of the sulphates there are two atoms of chromium in each molecule; hence we have the possibility of twelve unionized H_2O groups. The divalent radicle $(SO_4)''$ should replace two H_2O groups. Thus we can write for the hypothetical formulæ of the different sulphates:—

$$[\mathrm{Cr_2 12H_2O}](\mathrm{SO_4})_3$$

$$\left[\mathrm{Cr_2}^{\mathrm{10H_2O}}_{\mathrm{SO_4}}\right](\mathrm{SO_4})_2$$

$$\left[\mathrm{Cr_2}^{\mathrm{8H_2O}}_{(\mathrm{SO_4})_2}\right](\mathrm{SO_4})$$

$$\left[\mathrm{Cr_2}^{\mathrm{6H_2O}}_{(\mathrm{SO_4})_3}\right]$$

The first compound clearly represents the violet ionizing salt, the last being the non-ionizing green salt; the second may represent the lilac-grey sulphate having two-thirds of the $(SO_4)''$ in the precipitable condition, whilst the third may be the green sulphate which has one-third of its $(SO_4)''$ in the reactive condition.

The scheme of correlation suggested above explains many of the observed facts, and no doubt represents a close approximation to the truth. But it is to be noticed that in many cases the number of molecules of water found experimentally for the numerous salts exceed those required for the formation of the complex; thus the formula for the violet sulphate given above requires twelve molecules of water, whilst the violet sulphate, as we know it, has eighteen, the excess water being presumably loosely combined "water of crystallization." It is indeed stated that the violet salt, after being dried in sunlight, contains only twelve molecules of water, the six molecules of "crystal-water" being given off during the drying process.[1]

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[1] A. F. Joseph and W. N. Rae, *Trans. Chem. Soc.* **111** (1917), 196.

[2] G. O. Higley, *J. Amer. Chem. Soc.* **26** (1904), 613. See also J. Olie, *Zeitsch. Anorg. Chem.* **51** (1906), 29; W. R. Whitney, *Zeitsch. Phys. Chem.* **20** (1896), 64.

As already stated, the violet salts are more easy to crystallize than the green, and are therefore better known. One of the best developed is **chrome alum,** $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, which is conveniently prepared by reducing potassium dichromate ($K_2Cr_2O_7$) with sulphur dioxide; it crystallizes out in very dark purple octahedra, isomorphous with the other alums.

The hydrated **chloride** ($CrCl_3.6H_2O$) has already been referred to above as existing in two forms (violet and green); the **anhydrous chloride,** $CrCl_3$, is best prepared by passing dry chlorine over a mixture of chromic oxide and carbon heated in a hard-glass tube, and forms violet-red scales. The pure anhydrous chloride is dissolved so slowly by water as to appear practically insoluble. Actually, however, it has a high solubility limit. If a trace of chromous chloride be present, which acts as a catalyst for the dissolution process, the chromic chloride passes into solution quite readily and solutions of over 50 per cent. concentration can be obtained before the solubility limit is reached.

C. Compounds of Hexavalent Chromium (Chromic Acid and the Chromates).

When a chromic salt is treated in the presence of alkalis with hydrogen peroxide or other oxidizing agent, it is converted to an alkali salt of the higher oxide, CrO_3, which has a well-marked acidic character. For instance, if potassium hydroxide is added in excess to chromic sulphate solution and the mixture is treated with hydrogen peroxide, it becomes yellow and upon evaporation deposits yellow rhombic crystals of **potassium chromate,** K_2CrO_4. When the solution is acidified, the colour becomes orange, and, upon evaporation, yields—not, as might be expected, the ordinary acid salt $KHCrO_4$—but the anhydro-salt **potassium dichromate,** $K_2Cr_2O_7$ or $K_2CrO_4.CrO_3$, which is deposited in fine red triclinic crystals. Apparently this salt has a real existence in solution, ionizing into

$$2K^{\cdot} \text{ and } [Cr_2O_7]''.$$

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[1] M. Siewert, *Lieb. Ann.* 126 (1863), 101.

The orange colour of acidified solutions of chromates is thus due to the ion $[Cr_2O_7]''$ just as the yellow colour of neutral or alkaline solutions is due to the ion $(CrO_4)''$.

The red dichromate is considerably less soluble than the yellow chromate, and is therefore more easily prepared in a pure state. It is a stable compound and, unlike most compounds in a high state of oxidation, can be melted without decomposition. The melting-point is about 190° C. The solution has decided oxidizing properties; it converts, for instance, ferrous salts into ferric salts. It is reduced by sulphur dioxide to a chromic salt. The dichromate is also reduced by organic matter (e.g. gelatine or gum) when exposed to the light.

When further acid is added to a dichromate solution, the colour becomes a deeper orange. Anhydro-salts containing still greater quantities of chromic oxide are obtained by crystallizing strongly acidified solutions of chromates. For instance, a solution of the dichromate in hot nitric acid of specific gravity 1·2 deposits on cooling deep red crystals of **potassium trichromate,** $K_2Cr_3O_{10}$, while a similar solution in stronger nitric acid (specific gravity 1·4) yields the brown-red **potassium tetrachromate,** $K_2Cr_4O_{13}$.

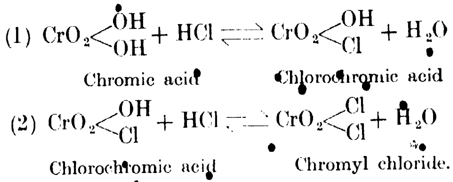
Chromium trioxide, CrO_3, from which the above salts are derived, can itself be isolated from a still more strongly acidified solution. To obtain the oxide, potassium dichromate is dissolved in 60 per cent. sulphuric acid, and the solution is allowed to deposit the crystals of potassium bisulphate ($KHSO_4$) which separate during the first twelve hours; if it is then mixed with a further quantity of concentrated sulphuric acid, a mass of scarlet crystals will slowly separate, which, after draining, can be washed free from the adherent liquid by means of pure nitric acid; the nitric acid is afterwards removed by drying the crystals in current of warm air, leaving chromium trioxide. The trioxide is a powerful oxidizing agent, and is less stable than potassium dichromate. It oxidizes alcohol very violently, when that liquid is dropped upon it; evolution of heat and light accompany the change. Chromium trioxide decomposes when heated at 250° C., evolving oxygen and yielding a lower oxide.

Solutions of chromium trioxide are orange-red and have powerful oxidizing properties. Solutions saturated at high temperatures deposit red crystals of the hydrate, H_2CrO_4, which may be regarded as the **chromic acid,** from which the chromates (e.g. K_2CrO_4) are derived; but the name "chromic acid" is usually applied to the anhydrous oxide, CrO_3. It appears probable, that, in the solutions of chromium trioxide, the chromium exists mainly as the highly ionized "dichromic acid" $H_2Cr_2O_7$, which corresponds to potassium dichromate $K_2Cr_2O_7$.

Ammonium **chromate** and **dichromate** are formed from solutions of chromic trioxide containing ammonia, the first being deposited when ammonia is in excess, and the second when chromic acid is in excess.

The **insoluble chromates** are obtained by precipitation. For instance **lead chromate,** $PbCrO_4$, is a yellow precipitate obtained on the addition of a potassium chromate solution to a solution of a lead salt; the same body is also formed if potassium dichromate is used instead of the chromate. It is dissolved by mineral acids, and also by alkalis. **Barium chromate** is a yellow precipitate, and **mercurous chromate** a scarlet precipitate obtained in an analogous manner. By the precipitation of silver nitrate with normal potassium chromate, brick-red **silver chromate,** Ag_2CrO_4, is obtained, but in this case potassium dichromate in weakly acid solution gives a dark-red precipitate of **silver dichromate,** $Ag_2Cr_2O_7$.

Chromic trioxide is almost devoid of basic properties; an oxychloride, CrO_2Cl_2, is known, which can be looked upon as a basic chloride of hexavalent chromium, but it is at once hydrolysed if brought into contact with water. It is known as **chromyl chloride,** and can be regarded as the product of reaction between chromic acid and hydrochloric acid. The reaction proceeds in two stages, both of them being reversible:—



$$(1)\quad CrO_2{<}^{OH}_{OH} + HCl \rightleftharpoons CrO_2{<}^{OH}_{Cl} + H_2O$$

$$(2)\quad CrO_2{<}^{OH}_{Cl} + HCl \rightleftharpoons CrO_2{<}^{Cl}_{Cl} + H_2O$$

When chromic acid is dissolved in strong hydrochloric acid, the reaction does not go beyond the first stage; but, if concentrated sulphuric acid (which, by absorbing the water produced, will favour the formation of chromyl chloride) is added in small qualities to the liquid, a heavy dark red liquid appears, and sinks to the bottom. This is chromyl chloride. It can be separated by means of a tap funnel, and freed from hydrogen chloride by drawing air through it.[1]

An older method of preparing the substance is by heating a mixture of sodium chloride and potassium dichromate with concentrated sulphuric acid. The sulphuric acid acts on the salts, yielding hydrogen chloride and chromium trioxide; and these two react together, the water produced being completely absorbed by the sulphuric acid. Chromyl chloride is therefore formed, and, being volatile, distils away; it may be collected in a well-cooled receiver.

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[1] H D. Law and F. M. Perkin, *Trans. Chem. Soc.* 91 (1907), 191.

Chromyl chloride is a very dark red liquid, boiling at 116° C. and producing a brown vapour of normal density. When introduced into water, it is almost at once hydrolysed into hydrochloric and chromic acids; if the water is present only in very small quantities, the hydrolysis is only partial, **chlorochromic acid,** which has been mentioned above, being produced.

The potassium salt of chlorochromic acid, $CrO_2{<}^{OK}_{Cl}$, is formed by warming potassium dichromate with concentrated hydrochloric acid; it separates from the solution in red tablets.

D. Intermediate Oxides (Chromium Chromates).

Various brownish or black compounds which can be looked upon as chromic chromates, $x Cr_2O_3 . y CrO_3$, are precipitated when a chromic salt is treated with a soluble chromate; similar bodies may be obtained by the action of chromic acid upon chromic hydroxide. Under certain conditions, the composition corresponds approximately to the formula $Cr_2O_3.CrO_3$ or CrO_2, and the product is often regarded as an intermediate oxide of chromium. The same body may be obtained as a dark grey powder in a dry way by heating chromic oxide in oxygen at 440° C.[1]

Another intermediate oxide, $2Cr_2O_3.CrO_3$ or Cr_5O_9, is best obtained by passing the vapour of chromyl chloride through a hot tube, in which it collects as a lustrous crust of little crystals belonging to the rhombic system. It is interesting to note that this oxide —like the intermediate oxide of iron and other metals—is distinctly magnetic.

E. Highly Oxidized Compounds of Chromium (Perchromic Acid and the Perchromates).

If a solution of chromium trioxide is treated with hydrogen peroxide, a deep blue coloration is obtained, containing a more highly oxidized substance. The blue solution, however, is extremely unstable, and rapidly gives off oxygen, a chromic salt being left, so that the ultimate effect of the action of hydrogen peroxide on a dichromate is a reduction, not an oxidation. But, if the blue solution obtained by adding hydrogen peroxide to a solution of chromic acid is at once shaken up with a little ether, the blue substance is extracted by the ether, being much more soluble in ether than in water. Now, in general, it is found that solutions in organic solvents react more slowly than aqueous solutions, and this is no exception to the rule; the ethereal solution decomposes much less readily than the aqueous solution and can be preserved for some time.

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[1] H. Moissan, *Ann. Chim. Phys.* **21** (1880), 245.

The blue solution appears to contain several highly oxidized bodies; although only one perchromic acid has been isolated in the solid state, salts and derivatives in three different states of oxidation are known. There has been a certain amount of disagreement regarding the nature of these bodies; but they may probably be regarded as derived respectively from

(*a*) $HCrO_5$ (unknown), which yields *violet* salts such as $KCrO_5.H_2O_2$, $NH_4CrO_5.H_2O_2$ and $HCrO_5.C_5H_5N$;
(*b*) CrO_4 (unknown), which yields *brown* derivatives such as $CrO_4.3NH_3$;
(*c*) H_3CrO_8 (known in a blue hydrated form), which yields *red* salts such as K_3CrO_8, $(NH_4)_3CrO_8$.

(*a*) **The salts of the acid $HCrO_5$**[1] are produced by treating the blue ethereal solution with alkaline substances at very low temperatures (below −5° C.), great care being taken to avoid any excess of alkali and to prevent any rise in the temperature. Thus on adding alcoholic potash to the blue solution, the potassium salt, $KCrO_5.H_2O_2$, separates as a violet precipitate; it is very unstable and decomposes if the temperature is allowed to rise even as high as 0° C.; like nitrogen iodide, it explodes when stirred. The ammonium salt, $NH_4CrO_5.H_2O_2$, is rather less unstable, and can be prepared by adding an ethereal solution of ammonia to the blue ethereal solution of perchromic acid at −5° C., excess of ammonia being carefully avoided; it is a violet-black crystalline powder, somewhat resembling pulverized potassium permanganate, and can be dried in a desiccator at 0° C. without decomposing. It decomposes, however, if exposed to the ordinary atmosphere. It is soluble in water, yielding a violet-brown solution. The *rôle* of the combined hydrogen peroxide in the molecule seems to be similar to that of water of crystallization in a hydrated salt.

Rather more stable salts, also derived from the acid $HCrO_5$, are obtained with organic bases, such as pyridine (C_5H_5N), piperidine ($C_5H_{11}N$) and aniline ($C_6H_5NH_2$); these contain no excess of hydrogen peroxide, and are violet or indigo substances, yielding brown solutions in organic solvents.

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[1] O. F. Wiede, *Ber.* 30 (1897), 2178; 31 (1898), 516, 3139; 32 (1899), 378; K. A. Hofmann and H. Hiendlmaier, *Ber.* 38 (1905), 3059, 3066.

(*b*) **Derivatives of the oxide CrO_4.** If the blue ethereal solution of perchromic acid is treated at a low temperature with *excess* of concentrated ammonia, a different body is formed. The excess of ammonia here acts as a reducer, and the aqueous layer, which becomes dark brown, deposits brown needles having the composition $3NH_3.CrO_4$. These needles explode if completely dried. This peculiar substance dissolves in a cool aqueous solution of potassium cyanide, giving a brown-red solution; on adding alcohol, an oil separates which finally deposits crystals, having the composition $3KCN.CrO_4$, and which explode when rubbed. The two substances $3KCN.CrO_4$ and $3NH_3.CrO_4$ appear to be addition products of an unknown oxide (CrO_4) with potassium cyanide and ammonia respectively.

(*c*) **The acid H_3CrO_8 and its salts** [1] are even more highly oxidized bodies than those hitherto described, although rather more stable.

The free acid is obtained by treating a suspension of chromic acid in methyl ether with concentrated (97 per cent.) hydrogen peroxide at very low temperatures, filtering from excess of chromic acid, and treating the liquid with phosphorus pentoxide to remove water. The solution is evaporated *in vacuo* at $-30°$ C., methyl ether being sufficiently volatile even at this low temperature; it leaves a dull blue residue having the composition $H_3CrO_8.2H_2O$. The acid decomposes at a perceptible rate even at $-30°$ C.; its "strength" is similar to that of acetic acid.

The corresponding salts are obtained by the action of concentrated hydrogen peroxide upon a faintly alkaline solution of a chromate. At low temperatures (below 0° C.), a solution of ammonium chromate containing excess of ammonia, when treated with hydrogen peroxide, deposits crystals of a red salt $(NH_4)_3CrO_8$, which can be washed with 95 per cent. alcohol and dried. The crystalline habit of the salt varies with the composition of the liquid from which it is obtained, and this has given rise to many apparently contradictory statements; but the composition—assuming the compound to be obtained pure—is always the same, unless the quantity of hydrogen peroxide present is insufficient; under such circumstances, the compound $CrO_4.3NH_3$, referred to above, is obtained. A red potassium salt, K_3CrO_8, is prepared in a manner analogous to the ammonium salt; it decomposes slowly when heated. When solutions of the red salts, $(NH_4)_3CrO_8$ and K_3CrO_8, are acidified at a low temperature, oxygen is evolved, and a blue solution, presumably containing the unknown blue acid, $HCrO_5$, is obtained.

[1] E. H. Riesenfeld, H. E. Wohlers and W. A. Kutsch, *Ber.* **38** (1905), 1885; E. H. Riesenfeld and W. Mau, *Ber.* **47** (1914), 548.

F. Miscellaneous Compounds.

Chromium Carbides.[1] Two carbides of chromium appear to exist. When chromium and excess of carbon are heated electrically in a crucible, the friable product contains numerous crystals having the composition Cr_3C_2; this carbide is remarkably stable both towards acids and alkalis. Another carbide, Cr_4C, is sometimes met with as needle-shaped crystals on the surface of the buttons of metallic chromium obtained by reducing the oxide with carbon.

Analytical

The changes of colour which accompany the oxidation and reduction of chromium compounds can be used to recognize their presence. Chromic salt solutions are normally violet, but become green when heated. When oxidized in alkaline solution with hydrogen peroxide, the yellow colour of a chromate appears. In acid solution, hydrogen peroxide yields a blue coloration due to perchromic acid. If a little ether is added, this test becomes quite sensitive; for not only is the blue perchromic acid less unstable in ethereal solution, but a few drops of ether will collect all the perchromic acid from a large volume of solution, and thus the blue colour can be detected, where otherwise it would not be recognized with certainty. Chromate solutions give yellow precipitates with lead acetate and with barium acetate, a brick-red precipitate with silver nitrate, and a reddish precipitate with mercurous nitrate. They are reduced to the green chromic salts when boiled with alcohol in acid solution.

In the ordinary method of analysis, chromium (if present as a chromic salt) is thrown down as a hydroxide by ammonia in the presence of ammonium chloride. Various other metals, like iron and aluminium, are precipitated in the same way, but it is possible to separate the chromium from these metals, by treatment with chlorine or bromine in the presence of caustic alkali. This converts the chromium to a soluble chromate; after boiling, and treatment with acid to dissolve the precipitate, the aluminium and iron may again be precipitated as hydroxides by means of ammonia, the chromium remaining in solution as a chromate.

Various methods are available for the final precipitation and weighing of the chromium. If free from sulphates, the nearly neutral solution can be precipitated with barium acetate, and the precipitate collected and weighed as barium chromate ($BaCrO_4$). Another convenient method is to treat the neutral or slightly acid solution with mercurous nitrate, when a red precipitate of mercurous chromate is formed. Although this substance has not a very constant composition, it yields green chromic oxide when heated, the volatile mercury passing away; chromium can then be weighed as Cr_2O_3. A third method of estimating chromium in a chromate is to reduce it to the trivalent condition by boiling with alcohol and acid and then to precipitate with ammonia as chromic hydroxide, which yields the anhydrous oxide upon ignition.

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[1] H. Moissan, *Comptes Rend.* 119 (1894), 185.

It is also possible to determine the strength of a chromate solution volumetrically. The easiest method is to add potassium iodide to the acidified solution and then to titrate the iodine liberated with a standard solution of sodium thiosulphate, starch being added as an indicator when the end-point is approached. It is best to dilute the solution considerably before titration, since otherwise the green colour of the chromic salt may be confused with the blue colour produced by iodine in the presence of starch.

TERRESTRIAL OCCURRENCE

The greater portion of the chromium present in an igneous magma, separates out among the earliest crystallizing constituents, as iron chromite, owing no doubt to the high melting-point of that compound, and its comparatively small solubility in the molten silicate mixture. Consequently, chromium is found mainly in basic rocks, and especially in ultra-basic rocks such as peridotite. The iron compound is a member of the spinel group of isomorphous minerals, and is known to mineralogists as

Chromite . . . $FeO.Cr_2O_3$.

Actually the composition of the mineral varies somewhat because the ferrous iron is replaced in part by magnesium, whilst the chromium is in part replaced by aluminium and also by (ferric) iron. Thus some specimens of so-called chromite tend to approach in composition the other members of the group, such as

Magnetite . . . $FeO.Fe_2O_3$
or Spinel . . . . $MgO.Fe_2O_3$

Chromite is black, lustrous and heavy, the specific gravity being about 4·4.

When ultra-basic rocks like peridotite undergo the form of decay known as "serpentinization," the chromite remains unchanged in the mass. Where the products of corrosion of a rock have been carried off by running water, the heavy grains of chromite are occasionally dropped in "placer" deposits not far from the place of origin.

Practically the whole of the world's supply of chromium and its compounds are derived from chromite, and the most valuable sources are those in which the rocks have undergone serpentinization, a change which usually renders the rock easier to work. An important quantity comes from serpentinized rocks of Rhodesia and Portuguese East Africa; a further supply comes from Baluchistan and Mysore, whilst a large quantity is mined in Oregon and California. Other deposits of importance occur in New Caledonia (in the same serpentine as the nickel), Quebec, Greece, and Cuba. It is of interest to note that there are also some small mines in the Shetland Islands.

Like vanadium, chromium is also found in small quantities in some of the ores of heavy metals. For instance, in the upper (oxidized) portions of lead ores, the insoluble chromate

Crocoite . . . $PbCrO_4$

often occurs as a red or orange mineral.

Traces of chromium also occur in numerous other minerals; where the mineral would otherwise be colourless, the presence of chromium will generally cause a colour, which will vary according to the state or oxidation and other circumstances. The green colour of emerald, the red colour of ruby, and possibly even the blue colour of sapphire,[1] are due (at least in some cases) to small quantities of chromium; but it seems likely that not all rubies and sapphires owe their colour to the same cause.

TECHNOLOGY AND USES

Although the greater proportion of the chromite mined is converted into ferrochrome and chromium chemicals, a considerable amount is used as a refractory material in furnaces. The comparatively high melting-point of chromite and its indifference to molten silicate mixtures has already been referred to. The special value of the material lies in the fact that—unlike most other refractory substances—it has neither marked acidic nor marked basic properties. If, for instance, a roof of siliceous material has to be constructed upon a furnace lined with basic material, it is sometimes convenient to separate the two materials by a layer of chromite, since if the siliceous roof rests directly on the basic substance, fluxing at the point of contact may occur. Recently, at some copper works, furnaces have been constructed in which the whole roof as well as the walls are composed of chromite.[2] The design of such furnaces is rendered difficult by the fact that chromite bricks tend to soften perceptibly at high temperatures.

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[1] A. Duboin, *Ber.* **31** (1898), 1977. But compare A. Verneuil, *Comptes Rend.* **151** (1910), 1063, who says that many sapphires contain no chromium, but owe their colour to the oxides of iron and titanium.

[2] W. H. Weed, *Min. Ind.* **28** (1919), 210.

Production of Chromates. The chromite ore is usually roasted under oxidizing conditions with sodium carbonate and lime at about 900–1,000° C., care being taken that the mass is only sintered and not actually fused. Under these circumstances the chromium is oxidized to the hexavalent state. Afterwards the roasted mass is extracted with water, usually containing more sodium carbonate, the leaching being preferably conducted in an autoclave under considerable steam pressure. The chromate is thus completely dissolved, whilst the iron remains behind as an insoluble oxide. On treating the yellow solution with sulphuric acid, it turns orange-red, showing the formation of **sodium dichromate** ($Na_2Cr_2O_7$); this salt can be prepared in the solid form by evaporating the liquid until sodium sulphate crystallizes out from the hot solution, and then cooling in order to obtain crystals of the dichromate. If the evaporation is conducted in iron vessels, care should be taken to have no excess of acid in the liquid, since free chromic acid acts on iron.[1]

If a dichromate is required in a state of purity, it is better to add to the solution potassium chloride, when **potassium dichromate** ($K_2Cr_2O_7$), which is much less soluble than the sodium salt, will separate out. Although the potassium salt can be obtained more pure, on account of its comparatively low solubility, it is clearly the most expensive of the two. The normal salts ($NaCrO_4$ and K_2CrO_4) are made by adding alkalis to the solutions of the dichromates.

The dichromates of potassium and sodium (commercially known as *bichromates*) are used for a number of purposes; in most cases, the employment depends on the oxidizing power of the salts. One quite unimportant use of the salts has been mentioned in Volume I—namely their employment as oxidizing depolarizers in the "bichromate cell." Far more important is the employment of potassium dichromate as an oxidizing agent in the manufacture of dye-stuffs. For instance, the oxidation of anthracene ($C_{14}H_{10}$) to anthraquinone ($C_{14}H_8O_2$), the basis of the red dye, alizarin or artificial madder,

$$C_{14}H_{10} + 3O = C_{14}H_8O_2 + H_2O,$$

can be brought about very easily by the action of potassium dichromate and sulphuric acid. The anthracene is heated with a concentrated solution of potassium dichromate and sulphuric acid, in lead-lined wooden tubs, until completely oxidized. In the process, the dichromate is reduced to the state of a chromic salt. From the liquid obtained, the volatile anthraquinone is removed by distillation in steam, and the solution left behind can be concentrated until chrome alum ($K_2SO_4.Cr_2(SO_4)_3.24H_2O$) is deposited. In some of the biggest dye-works, however (notably in Germany), the solution left is not evaporated, but is reconverted to dichromate by electrolysis. It is run directly into the anode compartment of a divided cell, a lead anode covered with lead peroxide being employed. Strictly speaking, it is the lead peroxide which produces the oxidation, being itself regenerated by the anodic action of the current. A current efficiency of 80 per cent. is obtained. Directly the oxidation is complete, the solution is run back into the lead-lined vats where it serves to oxidize a fresh portion of anthracene. By this regenerative method the chromium is not used up, but is alternatively oxidized by the electric current and reduced by the anthracene. Thus the oxidation of the anthracene is really conducted electrolytically, and both lead peroxide and potassium dichromate serve merely as " carriers " of oxygen.

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[1] G. Ulm, *Chem. Zeit.* 38 (1914), 670.

It has been mentioned that salt solutions of trivalent metals (e.g. aluminium) have a peculiar hardening action upon gelatine and similar bodies. Salts of trivalent chromium possess the property in a very marked degree, and many applications of chromium compounds depend on this fact. The " carbon " or " autotype " printing process used in photography, for instance, is based on the fact that gelatine containing potassium dichromate becomes insoluble when exposed to light ; for the light, in the presence of organic matter, reduces the chromate to a chromic compound (probably chromic hydroxide), and this hardens the gelatine, making it insoluble in hot water. The gelatine film used contains pigment, and is exposed to light through a negative ; then (after transference to another support) it is washed with hot water, which dissolves away the portions to which light has had no access. This leaves a positive image upon the support.

Chrome Tanning. Another application of the action of chromic salts upon gelatinous matter is the process of " chrome tannage,"[1] which has been developed mainly in America, but is now used very extensively in this country. It has already been mentioned that certain kinds of leather are made by soaking hides in baths containing aluminium salts ; the preparation of leather by means of trivalent chromium salts rests upon the same principle. The more obvious method consists in soaking the prepared hides in a chromic salt solution ; this is known as the " *one-bath process.*"

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[1] D. McCandlish, *J. Soc. Chem. Ind.* 38 (1919), 265T ; M. C. Lamb, *J. Soc. Chem. Ind.* 38 (1919), 266T.

Chrome alum, being a by-product of the alizarin industry, was the salt mainly used before the war in this country. It is necessary to make the solution slightly basic (by the addition of sodium carbonate) so as to deposit chromic hydroxide within the hide. On the other hand, it must not be too basic, or the chromium will never penetrate to the centre of the hide, which will remain untanned, although the surface will be over-tanned and "cracky." A little consideration will show the reason of this. The addition of a small amount of alkali will produce a certain amount of chromic hydroxide, but it will remain suspended as particles of colloidal size. As the liquor is made more and more basic the particles will tend to form aggregates until finally they form a true precipitate. The aggregates will clearly not penetrate the hide so easily as the small primary particles.

An alternative process, which avoids any difficulty that attaches to the securing of correct alkalinity is the "*two-bath process.*" Here the hides are drummed in a solution of chromic acid containing sodium chloride; the chromic acid quickly penetrates into the hide. It is then steeped in a bath containing a reducing agent such as glucose, sodium thiosulphate or sodium bisulphite which precipitates chromic hydroxide within the hide. The "two-bath process" is normally used for treating goat-skins in the manufacture of "glacé kid." During the war it was used also for other purposes, owing to the shortage of chrome alum, and the exceptional demand for chrome leather, which was considered preferable for "marching-boots." At present practically the whole of the leather used for better quality boot "uppers" is tanned with chromium, and is afterwards impregnated with a mixture of sulphonated oils which act as a lubricant and render the leather supple.

Chrome tannage is very much more rapid than the older vegetable tannage; according to McCandlish, "it can be completed in as many hours as the former process required days." This rapidity is, to the practical tanner, one of the main points in favour of the new method.

It is interesting to note that chrome tanning, unlike ordinary tanning, is a reversible process. If a chrome-tanned leather is soaked in a solution of a tartrate like "Rochelle salt" (sodium potassium tartrate) which has a considerable solvent power for chromic hydroxide, the hide returns to a condition similar to that of an untanned hide, and the chromium is recovered. This discovery is not without practical importance.[1]

Chromium Pigments. Several of the insoluble chromates are useful yellow pigments. Most important is lead chromate

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[1] H. R. Proctor and J. A. Wilson, *J. Soc. Chem. Ind.* 35 (1916), 156.

($PbCrO_4$), known as "*chrome yellow*," which is obtained by the precipitation of a lead salt with potassium dichromate. The colour varies with the temperature of precipitation, being darker when obtained from a hot solution. This difference is probably mainly due to the difference in the size of the particles. As pointed out in the introduction (Vol. I, page 98), a coloured substance always appears deeper in tint when present in large grains than when present in small ones. In general, crystal-particles are likely to be bigger when produced from a hot solution than when produced from a cold solution; for the "degree of supersaturation" at the moment of mixing will be less in the hot solutions, and the number of nuclei produced is therefore likely to be smaller.[1]

When chrome yellow is treated with caustic soda, a reddish basic lead chromate (said to be $PbCrO_4.PbO$) known as *chrome red* is obtained; in this case, the change of colour is due to change of chemical composition, and not due to the physical state. A basic zinc chromate obtained by precipitating hot neutral zinc sulphate with potassium chromate is also used as a pigment under the name *zinc yellow.*

Chromic oxide (Cr_2O_3) forms a valuable green pigment. Here again, the colour varies with the mode of preparation. When obtained by heating ammonium dichromate a fine colour is obtained. A cheaper method is to heat potassium (or sodium) dichromate with sulphur, and to wash the product free from caustic alkali; the product is less satisfactory as a pigment, but serves for use in glass. If potassium dichromate is fused with boric acid, a potassium chromic borate is obtained, which, on treatment with water, hydrolyses, yielding a variety of chromic hydroxide possessing a fine green colour. The product, which is known as *Guignet's green,* almost invariably contains some boric acid, and may be regarded, if preferred, as a basic chromium borate.[2]

Chrome green, along with zinc borate and linseed oil, is a constituent of a preparation recently recommended in America for the fire-proofing of wood.[3]

Chromium in Steel. Probably the most important demand for chromium is for use in the manufacture of special steels. It is not added in the pure state to the molten steel, but as an alloy of iron and chromium known as *ferrochrome*, which, like most ferro-alloys, is made in the electric furnace by reducing the oxides of iron and chromium with carbon. The presence of a small quantity of chromium has an important specific effect on steel. Chrome vanadium steel, being both hard and strong, is now used in the construction of locomotive wheels, axle-shafts, gears and springs; its properties can be varied to an astonishing extent by proper heat-treatment. Chrome-nickel steel is used in automobile construction, as well as for armour-plate and the tips of shells; it is excellent for case-hardening. Chrome-tungsten steel or chrome-molybdenum steel is used for high-speed tools. Lastly, many stainless cutlery steels contains chromium.

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[1] Compare E. E. Free, *J. Phys. Chem.* **13** (1909), 121, who also discusses the variation of colour with the concentration of the precipitating solutions—a subject regarding which the facts are less easy of interpretation.

[2] See also F. Rose, "Mineralfarben" (Spamer).

[3] *J. Soc. Chem. Ind.* **39** (1920), 379R.

All these materials will be discussed further in the section on steel (Vol. III). *Nichrome,* an important alloy of chromium and nickel, is referred to in the section on nickel, whilst *stellite,* another alloy containing chromium, is mentioned in the section on cobalt.

Other Uses of Chromium. As already stated, chromium salts are used as colouring agents in the manufacture of glass and in the ceramic industry. The colour produced varies with the state of oxidation, the state of aggregation and composition of the material to which the chromium is added; in ceramics, chromium normally produces a green colour, but in alkaline glazes it causes a yellow colour (no doubt due to chromates, which become stable in the presence of alkali).

Chromium salts are, like aluminium salts, used as mordants in dyeing.

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MOLYBDENUM

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The Metal

Molybdenum resembles chromium in general properties. It is a silver-white metal, taking a good lustre; the pure metal is fairly malleable when hot and only moderately hard, but it is rendered much harder by the presence of carbon. Like chromium it has an exceedingly high melting-point (2,450° C.).

Although superficially oxidized at high temperatures the metal is not perceptibly altered by exposure to the atmosphere at ordinary temperatures, except in the very finely divided condition. Probably there exists upon it a protective oxide-film. The metal, no doubt for a similar reason, is not readily dissolved by acids, although nitric acid, concentrated sulphuric acid and hydrofluoric acid attack it perceptibly. It is easily brought into the "passive" state, either by anodic treatment, or by immersion in oxidizing agents, such as chromic acid. It is noteworthy that treatment in 20 per cent. hydrochloric acid renders active molybdenum passive, whilst treatment with potassium hydroxide is most effective in restoring the activity.[1] These facts—which represent the exact converse of the state of affairs met with in the case of iron and nickel—are at once understood if it is agreed that the passivity is due to an oxide film. The oxide of molybdenum is soluble in alkali (forming a molybdate), but not freely soluble in acid; the oxides of iron and nickel are soluble in acid but not in alkali.

The anodic behaviour of molybdenum is of some little interest. A molybdenum anode surrounded by a bath containing sodium hydroxide or hydrochloric acid passes readily into solution. But if iodides are present in the solution, the production of free iodine takes place as well as the dissolution of molybdenum.[2] In the case of a chromium anode, it will be remembered, potassium iodide has a similar effect in lowering the current efficiency of anodic dissolution, the effect being actually more complete than in the case of molybdenum.

In the absence of iodides, the anodic dissolution proceeds fairly readily; in alkaline solutions, the amount dissolved agrees, at low current-densities, with that calculated from Faraday's Law on the assumption that molybdenum passes into the solution in a hexavalent condition (producing a molybdate). But if the current density becomes too high, oxygen is evolved, the molybdenum becomes passive, and the current efficiency drops off; this occurs more readily at low temperatures than in a warm solution.

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[1] W. Muthmann and F. Fraunberger, *Sitzungsber. Bayer. Akad.* **34** (1904), 217.

[2] L. Marino, *Gazetta* **35** (1905), ii. 193. See also H. Kuessner, *Zeitsch. Elektrochem.* **16** (1910), 754.

Laboratory Preparation. It is possible to prepare molybdenum from the trioxide on a small scale by means of the "thermite reaction," aluminium being used as reducing agent; the addition of liquid air to the mixture of molybdenum oxide and excess of aluminium has been advocated in order that the temperature may be raised, during the reaction, well above the melting-point of the molybdenum. However the yield is always low owing to the volatility of the trioxide.[1]

When molybdenum oxide is heated with carbon in the electric furnace a better yield of metal is obtained, but the product is apt to contain carbon. It is possible to obtain the metal in a purer state by heating the oxide in a current of hydrogen. If the trioxide (MoO_3) is the material employed it is first reduced to a lower oxide by heating in hydrogen in a glass tube, care being taken not to allow the temperature to rise unduly high and thus cause loss of the volatile trioxide by sublimation. The lower oxide is then heated, far more strongly in hydrogen in a porcelain tube, and is thus reduced to the metallic state; the hydrogen must be dry and free from oxygen. The operation is continued until no more water vapour is carried off by the gas-stream.[2] The product, however, still contains traces of oxygen, which can only be removed by heating for several hours in a current of hydrogen at a temperature of 2,250° C.; when quite free from oxide, the finely divided metal can be pressed quite easily into sticks.[3]

Compounds

Most of the best developed compounds of molybdenum correspond to the trioxide (MoO_3), which has marked acidic—and feeble basic—properties, being in many respects similar to the analogous chromium trioxide (CrO_3). A dioxide (MoO_2) and sesquioxide (Mo_2O_3) are known; they have apparently weak basic properties. There are also a few compounds corresponding to the oxide MoO. Intermediate oxides (Mo_2O_5, and Mo_3O_8), as well as various peroxides, have been prepared. It will be convenient to describe the derivatives of the stable trioxide (MoO_3) first.

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[1] A. Stavenhagen, *Ber.* **32** (1899), 3065.

[2] See H. Moissan, "Traité de Chimie Minérale" (Masson), Vol. IV.

[3] K. Wolf, Dissertation, Aachen (1918); Abstract, *J. Chem. Soc.* **114** (1918), ii. 350.

A. Compounds of Hexavalent Molybdenum.

The **trioxide**, MoO_3, is formed, when the finely divided metal or one of the lower oxides is heated strongly in air. It is more conveniently prepared by roasting the disulphide (MoS_2), or by igniting ammonium molybdate. Unlike the chromium analogue, it is colourless at lower temperatures, although it becomes yellow when heated. It is fusible at a red heat, yielding a red-yellow liquid, and is distinctly volatile even below the melting-point. It can therefore be purified by sublimation, preferably conducted in platinum vessels, since the use of porcelain generally causes the sublimate to be contaminated with silica and alumina. The sublimed oxide is very voluminous.

The hydrated oxide, generally known as **molybdic acid**, $H_2MoO_4.H_2O$, is produced as a white or yellow crystalline mass, when a solution of a molybdenum salt is allowed to hydrolyse spontaneously, or when a solution of ammonium molybdate is decomposed with nitric acid. If, however, the molybdate solution is very dilute, and is decomposed, preferably, with hydrochloric acid, no precipitate will be seen, and, after removal of the ammonium chloride and excess of hydrochloric acid by dialysis, a colloidal solution of molybdic acid is left, which can be evaporated without flocculation. This concentrated colloidal solution is, as usual, flocculated by the addition of an electrolyte. If the solution is evaporated sufficiently, a gummy residue is obtained; when completely dried by standing over sulphuric acid, it is stated to have the composition $H_2Mo_2O_7$.

The **molybdates** are formed when the trioxide is fused with alkalis, or with alkaline carbonates, or dissolved in a solution of an alkali. The soluble salts are for the most part colourless. The tendency to form anhydro-salts is even more marked than in the case of the chromates. For instance sodium **normal molybdate** (Na_2MoO_4), **dimolybdate** ($Na_2Mo_2O_7$), **trimolybdate** ($Na_2Mo_3O_{10}$) are all obtained by fusing the trioxide with the requisite quantity of sodium carbonate, and purifying the product by recrystallization. By the addition of the proper amount of acid to solutions of the normal molybdate, followed by crystallization, the **tetramolybdate** ($Na_2Mo_4O_{13}$), **octamolybdate** ($Na_2Mo_8O_{25}$) and **decamolybdate** ($Na_2Mo_{10}O_{31}$) can be obtained.[1] The potassium salts are prepared in an analogous way. When a solution of molybdenum trioxide in ammonia is crystallized, the salt normally obtained is the so-called "**common ammonium molybdate,**" $(NH_4)_6Mo_7O_{24}.4H_2O$. Various other ammonium molybdates, obtainable by crystallization from distinctly acid or distinctly ammoniacal solutions, are also known.

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[1] G. Wempe, *Zeitsch. Anorg. Chem.* 78 (1912), 298. Consult also the views of A. Rosenheim and J. Felix, *Zeitsch. Anorg. Chem.* 79 (1913), 292.

The insoluble molybdates are obtained, as usual, by precipitation. Those of calcium and barium are white. **Lead molybdate,** $PbMoO_4$, is practically white when obtained by precipitation; but, if produced by fusing solid lead chloride with sodium molybdate and sodium chloride, it is distinctly yellow, although possessing, apparently, the same composition. No doubt, the correct explanation is similar to that given to account for the variation in colour of lead chromate, the hot process yielding crystals of moderate size, whilst the ultimate particles of the cold process are extremely small.

The most remarkable feature of molybdenum trioxide is the series of addition-products which it forms with orthophosphates. These are known as **phospho-molybdates** and are yellow insoluble bodies, usually containing 12 molecules of MoO_3 to every $(PO_4)'''$ group. For instance, on adding excess of ammonium molybdate to a dilute solution of phosphoric acid containing nitric acid, a yellow crystalline precipitate of **ammonium phospho-molybdate,** $(NH_4)_3PO_4.12MoO_3$, is produced. This is dissolved by ammonia, and by crystallizing the solution, more soluble (colourless) salts containing a smaller proportion of molybdenum trioxide are obtained, e.g. $2(NH_4)_3PO_4.5MoO_3.7H_2O$. Ammonium phospho-molybdate is undissolved by ordinary acids; but aqua regia attacks it slowly, yielding a solution from which various phospho-molybdic acids, containing P_2O_5, MoO_3 and H_2O in different proportions can be obtained by crystallization.

As has already been stated, molybdenum trioxide has feeble basic, as well as acidic properties. When a solution of a molybdate is treated with sulphuric acid of moderate concentration, the molybdic acid, precipitated in the first instance, redissolves in excess of sulphuric acid, yielding a colourless solution. Even the anhydrous oxide, MoO_3, dissolves in hot concentrated sulphuric acid. It is not possible to obtain solid normal salts from the solution, but a **basic sulphate,** MoO_2SO_4, and a volatile **basic chloride,** MoO_2Cl_2, have been isolated. The chloride, $MoCl_6$, has never been obtained even in the dry way, but a **fluoride,**[1] MoF_6, is prepared by the action of fluorine on metallic molybdenum at 60–70° C.; the finely divided metal is placed in a long platinum tube and a current of fluorine is passed through the tube, which carries forward the hexafluoride into a dry glass vessel cooled to −70° C. in a carbon dioxide-alcohol mixture. The fluoride is a white solid at low temperatures, but melts at 17° C., boils at 35° C., and is hydrolysed by water, suffering at the same time reduction to the blue lower oxide.

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[1] O. Ruff and F. Eisner, *Ber.* **40** (1907), 2926.

An important insoluble salt of hexavalent molybdenum is the **sulphide**, MoS_3, which is obtained as a brown precipitate on passing hydrogen sulphide gas through a solution of ammonium molybdate to which hydrochloric acid has been added. Like the sulphides of tin, antimony and arsenic, it is dissolved by alkaline sulphides, and from the red solutions thus produced, red crystals of the thiomolybdates are obtained. **Potassium thiomolybdate**, K_2MoS_4, for instance, can be crystallized from a solution of molybdenum trisulphide (MoS_3) in aqueous potassium sulphide, or from a solution of potassium molybdate saturated with hydrogen sulphide; it forms deep red tablets.

B. Intermediate Oxides of Molybdenum ($MoO_2.nMoO_3$), and Derivatives.

When a solution of a molybdate is reduced with sulphur dioxide or stannous chloride, a blue solution is obtained. If the reduction is brought about by zinc, the same blue colour is produced, but in this case, the reduction proceeds further; if time is allowed, the blue colour will change to brown and finally to black, compounds of tetravalent or trivalent molybdenum being produced. The blue solution must be regarded essentially as a colloidal solution of a blue oxide.[1] The blue oxide is often deposited spontaneously when the solution is allowed to stand, but the formation of the solid is hastened by evaporation, or by the addition of concentrated hydrochloric acid. The composition is generally considered to be Mo_3O_8, although it varies somewhat with the conditions of preparation. It is probably correct, however, to regard it as a **molybdenum molybdate**, formed by the combination of MoO_2 and MoO_3 in various proportions, for it can also be produced by precipitating the solution of a salt of tetravalent molybdenum with ammonium molybdate.

A method of obtaining the blue oxide free from electrolytes consists in treating a suspension of the trioxide (MoO_3) with metallic molybdenum. A blue liquid is obtained, which yields a solid oxide approximating to the composition Mo_3O_8 or $MO_2.2MoO_3$.

When treated with hydrogen chloride gas, the blue solution deposits the blue oxide, as stated above; excess of hydrogen chloride, however, causes it to split up into molybdic acid, and a lower chloride (probably $MoCl_5$), which imparts a yellow-brown or green colour to the liquid.[1]

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[1] A. Dumanski, *Koll. Zeitsch.* 7 (1910), 20.

When a hot solution of molybdenum trioxide in concentrated sulphuric acid is reduced with hydrogen sulphide, the liquid becomes first blue and then green, depositing as it cools dark green crystals of the composition $Mo_2O_5.2SO_3$, which are only slowly soluble in water.[2]

C. Compounds of Tetravalent Molybdenum.

The **dioxide**, MoO_2, is formed when the trioxide is heated for some hours in hydrogen at 470° C. The heating must not be too strong, or the trioxide will sublime away unchanged. Any trioxide which remains in the product may be removed by heating in a current of hydrogen chloride which converts it into the highly volatile oxychloride, MoO_2Cl_2. The dioxide is a brown crystalline substance when pure, but is frequently coloured blue or violet through contamination with other oxides. A dark red **hydroxide,** $Mo(OH)_4$, resembling ferric hydroxide, is produced when the salts are precipitated with ammonia; there is a marked tendency towards the formation of colloidal solutions.

Possibly because the anhydrous oxide is usually prepared at a high temperature, it dissolves only with difficulty in acids. Salts of tetravalent molybdenum are, however, thought by chemists to be formed in solution upon the reduction of the salts of hexavalent molybdenum with zinc. As has been stated, reduction with zinc causes the colour to become first blue, then green or brown, then brown-black. It is generally considered that the green or brown stage corresponds to the salts of tetravalent molybdenum, although —as has already been pointed out—greenish compounds have been isolated in which the molybdenum appears to be pentavalent.

The most important insoluble compound of tetravalent molybdenum is the **sulphide,** MoS_2, which is preferably prepared in the dry way, by fusing the trioxide with sulphur. It is a black or lead-grey substance having a metallic lustre, and is one of the most stable of molybdenum compounds, as is illustrated by the fact that it is the form in which molybdenum is commonly found in nature.

D. Compounds of Trivalent Molybdenum.

The final effect of the action of zinc upon salts of the trioxide (MoO_3) is the production of a brown-black solution, which seems to contain salts of trivalent molybdenum. The **hydroxide**, $Mo(OH)_3$, is obtained by precipitation with ammonia as a brown precipitate, and leaves the black anhydrous **oxide** when carefully ignited. Both oxides and salt solutions become oxidized when exposed to the air. The soluble salts cannot be isolated.

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[1] M. Guichard, *Ann. Chim. Phys.* 23 (1901), 537; *Comptes Rend.* **143** (1906), 744.

[2] Lailhache, *Comptes Rend.* **132** (1901), 475.

The trihydroxide is also formed in small quantities as a deposit on the cathode when a solution of a higher molybdenum compound is electrolysed.

The corresponding **sulphide**, Mo_2S_3, has been produced by heating the disulphide in the electric furnace.

E. Compounds of Divalent Molybdenum.[1]

The preparation of the yellow **chloride**, $MoCl_2$, is described below along with the other chlorides. It yields a yellow solution in sodium hydroxide, which on boiling deposits a black precipitate of the **hydroxide**, $Mo(OH)_2$.

F. Highly Oxidized Compounds of Molybdenum.

When a molybdate, or molybdenum trioxide, is treated with hydrogen peroxide, a yellow solution is produced, which contains a permolybdate or permolybdic acid. Some of these, including the free acid H_2MoO_5, and the **potassium molybdate-permolybdate**, $K_2MoO_5.2MoO_3.3H_2O$, have been isolated in the solid state, preferably by evaporation *in vacuo*.

Persulphides of molybdenum and their derivatives are also known. When potassium dimolybdate($K_2Mo_2O_7$) is saturated with hydrogen sulphide, one would expect to get MoS_3 or K_2MoS_4. Actually, however, one obtains a mixture of lower sulphides together with a compound richer in sulphur, namely the red **per-thiomolybdate**, $KHMoS_5$, which happens to be rather insoluble. By the action of hydrochloric acid, the corresponding **per-thiomolybdic acid**, H_2MoS_5, is obtained, which yields the brown **tetrasulphide**, MoS_4, on heating.

Compounds derived from an even higher sulphide (Mo_2S_{11}) are formed by the action of yellow ammonium sulphide (containing polysulphides) upon solutions of ordinary thiomolybdates. The potassium salt, $KMoS_6$, separates in brown crystals which yield the acid, $HMoS_6$, on treatment with hydrochloric acid.

G. Miscellaneous Compounds.

Chlorides of Molybdenum.[1] Since the chlorides of molybdenum cannot be isolated from solutions of the various oxides in hydrochloric acid, they must be considered separately. The hexachloride ($MoCl_6$) is unknown, although the corresponding fluoride has been isolated. The **pentachloride**, $MoCl_5$, is obtained by the action of pure chlorine on the heated metal; the metal used must be absolutely free from oxygen, or oxychlorides will be produced. It is a black crystalline substance which yields a red vapour of normal density when heated. When heated in a current of hydrogen at 250° C., it decomposes, the red **trichloride**, $MoCl_3$, being formed. If the trichloride is heated in a current of carbon dioxide, it also breaks up into the dichloride and tetrachloride; of these the volatile **tetrachloride**, $MoCl_4$, passes away, and can be collected as a brown powder in a cooled receiver, while the pale yellow **dichloride**, $MoCl_2$, remains behind.

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[1] K. Wolf, Dissertation, Aachen, Abstract, *J. Chem. Soc.* **114** (1918), ii. 350

Carbides.[1] It is well known that molybdenum prepared by means of carbon is apt to contain carbon, which causes considerable modification of properties, rendering it darker, harder and more brittle. The metallography of the molybdenum-carbon alloys has not been fully worked out, but it is stated that two definite carbides, MoC and Mo_2C, exist. They are lustrous, crystalline bodies, white or grey in colour. A hard double carbide, Fe_3Mo_3C, occurs as an important constituent of molybdenum steels.

Carbonyl.[2] The volatile carbonyl of molybdenum is of especial interest in view of the formation of similar carbonyls by metals like iron, cobalt, nickel and ruthenium, which will be considered shortly. It is, however, not produced easily, a special retort capable of standing high pressures being required. When finely divided molybdenum is heated at 200° C. in a stream of carbon monoxide under a pressure of over 150 atmospheres, the gas carries off a small quantity of molybdenum carbonyl, which can be condensed as white crystals, if the gas is allowed to pass out through a well-cooled glass tube. The crystals can be sublimed in an atmosphere of hydrogen or carbon monoxide at 30–40° C.; they have a composition which is most nearly represented by the formula $Mo_6(CO)_{26}$, although the discoverers assigned the formula $Mo(CO)_6$ to the carbonyl.

Analytical

Solutions of molybdates, previously acidified, give a yellow precipitate with sodium phosphate, and are coloured first blue, then green or brown, and lastly brownish-black when treated with zinc. Other tests for molybdenum are based on the precipitation of various insoluble molybdates, by interaction with salts of lead, barium or mercury.

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[1] H. Moissan and K. Hoffmann, *Comptes Rend.* **138** (1904), 1558; H. Moissan, *Comptes Rend.* **120** (1895), 1320.

[2] L. Mond, H. Hirtz and M. D. Cowap, *Trans. Chem. Soc.* **97** (1910), 798; R. L. Mond and A. E. Wallis. *Trans. Chem. Soc.* **121** (1922), 29.

A very sensitive test for molybdenum depends upon the addition of potassium thiocyanate, followed by a small piece of zinc, to the solution under examination. If ferric iron is present a blood-red colour may appear before zinc is added; but the reduction caused by the zinc soon removes the colour due to iron; if molybdenum is present, a crimson coloration, probably due to $Mo(SCN)_3$, appears after a few seconds. The test is most sensitive if the solution is nearly neutral.[1]

The trioxide of molybdenum has but feeble basic properties, and molybdic acid is easily precipitated by the addition of an acid to a solution of a molybdate. Thus there is but little difficulty in separating molybdenum from the more basic metals. On the other hand, the separation of molybdenum from other elements with acid-forming oxides is more difficult. The separation from tungsten is specially important. One method depends on the fact that molybdic acid (in the freshly precipitated state) is dissolved by sulphuric acid of specific gravity 1·378 when warmed, whilst the tungstic acid remains undissolved, the basic properties of the trioxide being even more feeble in the case of tungsten than in the case of molybdenum.[2]

The separation from vanadium depends on the precipitation of molybdenum as the trisulphide (MoS_3) when hydrogen sulphide is passed through a solution containing both vanadates and molybdates, acidified with sulphuric acid. The sulphide can be filtered off, ignited cautiously and weighed as the trioxide MoO_3. Care must be taken not to raise the temperature too high, since the trioxide is volatile at a bright red heat.

In general, after the separation of other metals, the molybdenum is brought to the state of a molybdate, and is then precipitated with mercurous nitrate. The mercurous molybdate produced is ignited gently so as to drive off mercury, and the residue is weighed as MoO_3.

A volumetric method of estimating molybdenum depends on reduction to the pentavalent state by means of potassium iodide in the presence of hydrochloric acid and subsequent titration with potassium permanganate. For details the original paper should be consulted.[1]

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[1] J Moir, *J. Chem. Met. Min. Soc., S. Africa*, 16 (1916), 191.

[2] M. J. Ruegenberg and E. F. Smith, *J. Amer. Chem. Soc.* **22** (1900), 772. According to F. P. Treadwell ("Analytical Chemistry") concentrated sulphuric acid should be used for the digestion of the oxides and then diluted with three parts of water.

TERRESTRIAL OCCURRENCE

Molybdenum and the two succeeding elements, tungsten and uranium, are associated commonly with the acid rocks such as granite, and thus present a contrast to chromium, which occurs in basic rocks. This "magmatic opposition" between chromium and its homologues is somewhat remarkable, but there is an analogous case in the previous group; for vanadium is found mainly in basic rocks, whilst niobium and tantalum occur in siliceous rocks.

Besides their occurrence within the granitic rock itself, molybdenum minerals are frequently found in quartz lodes and pegmatite dykes that spring from acid intrusive masses.[2] In other cases, the origin of the molybdenum minerals must be attributed to the impregnation of the country rock by molybdenum-bearing waters, no doubt also originating from an intrusive mass.

The most important mineral is the sulphide,

Molybdenite . . . . MoS_2,

which occurs in crystals or fine flakes and granules, having a greyish metallic lustre similar to that of graphite. In the oxidized portions of the veins or rocks, the weathering of molybdenite and pyrites has given rise to the hydrated molybdate,

Molybdic ochre, perhaps, $2Fe_2(MoO_4)_3.15H_2O$.

The formula given above must be accepted with caution, since the composition is variable. The ochre is sometimes described as molybdenum oxide, but the iron appears to be an essential constituent.[3]

The most important molybdenite ores occur in Australia (Queensland and New South Wales), Canada (Quebec), the United States and Norway.

Lead molybdate is also found in nature, being known as

Wulfenite . . . . . $PbMoO_4$.

It is a yellow mineral, often more or less transparent, and having an adamantine lustre.

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[1] F. A. Gooch and O. S. Pulman, *Amer. J. Sci.* **12** (1901), 449. Another volumetric method of estimating molybdenum, depending on reduction by zinc, is described by J. P. Bonardi and E. P. Barrett, *U.S. Bur. Mines*, Technical Paper, **230** (1920).

[2] See E. Thomson, *Econ. Geol.* **13** (1918), 302, who described three different types of deposits. Also F. W. Horton, *U.S. Bur. Mines, Bull.* **111** (1916).

[3] W. T. Schaller, *Amer. J. Sci.*, **23** (1907), 297.

TECHNOLOGY AND USES

Of the minerals just mentioned, the sulphide has most importance as a source of molybdenum, although wulfenite also has been employed in the United States.

In some cases, other metals occur along with molybdenum; the Australian deposits, for instance, which supplied 70 per cent. of the world's needs up to the time of the war, contain tungsten and bismuth.[1]

In most cases, the molybdenite occurs in comparatively small flakes or granules embedded in a quartz-reef or distributed through granite or pegmatite. Thus in nearly every case some sort of concentrating plant must be installed, preferably near the mine, which will eliminate part at least of the valueless matter, and produce a material rich enough to be sent to the smelter. The process of concentration employed will clearly depend upon the character of the gangue minerals, but by far the most usual system of concentration is that of **flotation**.[2] For many ores, the **Elmore vacuum process**[3] appears especially suitable. The ore is finely ground in a ball-mill with a small quantity of pine-oil and kerosene, and the pulp produced passes on to the mixer A (Fig. 17), whence it flows continually into the funnel B and is sucked through the pipe C into the vessel D, in which a vacuum is maintained by means of an exhaust pump. The reduced pressure causes the air dissolved in the water to be liberated as bubbles, and consequently a froth appears in the upper part of

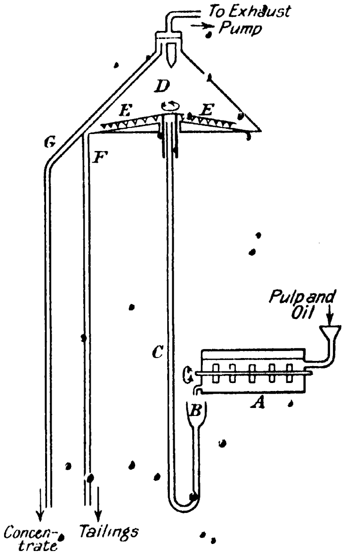

FIG. 17.—Principle of the Elmore Vacuum Flotation Plant.

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[1] S. J. Johnstone, *J. Soc. Chem. Ind.* **37** (1918), 441R.

[2] C. E. Oliver, *Eng. Min. J.* **109** (1920), 840; H. H. Claudet, *Eng. Min. J.* **103** (1917), 786; *Trans. Canadian Min. Inst.* **19** (1916), 124; **20** (1917), 121; E. R. Woakes, *Trans. Inst. Min. Met.* **27** (1918), 184.

[3] See T. J. Hoover, "Concentrating Ores by Flotation" (published by the Mining Magazine) (1916), Ch. VIII.

the vessel. In the froth, each bubble of air is surrounded by a thin film of oil. The particles of molybdenite cling to the oil films surrounding the bubbles, and thus remain suspended in the froth, whilst the gangue particles sink to the bottom of the vessel. The rakes E attached to a rotating shaft gradually work the worthless particles at the bottom to the edge, and they pass out through the pipe F, whilst the froth, bearing the precious molybdenite particles, overflows continuously and emerges through the pipe G.

This process is worked successfully in Norway. Where the ore contains other sulphides, such as pyrites—as in Canada—there is a tendency for these other sulphides to adhere to the froth as well as the molybdenite. It has, however, been found possible to separate molybdenite from pyrites also, by flotation under appropriate conditions.

Molybdenum in Steel. Most of the molybdenum concentrates are used for the manufacture as the alloy with iron known as **ferro-molybdenum,** which is largely used as an addition to steel. It was at one time usual to roast the sulphide to oxide, and then to reduce the oxide with carbon in the electric furnace, iron or iron oxide being added to the charge. The roasting of molybdenites, however, presents difficulties owing to the volatility of the oxide.[1] It is perfectly possible to reduce the sulphide without roasting, by mixing lime with the charge [2]; practically the whole of the sulphur passes into the slag as calcium sulphide according to the equation,

$$MoS_2 + 2CaO + 2C = Mo + 2CaS + 2CO.$$

This process is actually used, in Canada and elsewhere, for the manufacture of ferro-molybdenum.

High-speed tool steels containing molybdenum are very similar to those containing tungsten, but for a long time tungsten was the metal mainly used for the purpose, because molybdenum steel gave trouble owing to "seaminess" and liability to crack. During the war, however, there was a shortage of tungsten, and molybdenum steel was largely employed. It seems that the main difficulties concerning the production of molybdenum steel in sound ingots have been overcome, and that molybdenum steel will in future have an importance at least equal to that of tungsten steel.

Metallic Molybdenum is also made to some extent by a similar process, namely the reduction of the oxide in the electric furnace. Where extreme purity is not required, reduction of the oxide with carbon, or of the sulphide with carbon and lime, is possible. It is stated that molybdenum containing carbon can be purified by heating with the oxide. A method of obtaining pure metal depends on heating the purified oxide in hydrogen in the electric furnace; the product is then crushed and screened, and again heated at 1,200° C. for some hours. The metallic powder can now be pressed together in a mould to form a coherent mass, which is "sintered" by heating electrically, and finally heated very strongly *in vacuo*. This yields compact molybdenum.

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[1] A. Stansfield, *J. Inst. Met.* **15** (1916), 287.

[2] O. W. Brown, *Trans. Amer. Electrochem. Soc.* **9** (1906), 109; R. M. Keeney, *Trans. Amer. Electrochem. Soc.* **24** (1913), 167; J. W. Evans, *Trans. Canadian Min. Inst.* **21** (1918), 154.

Molybdenum is not naturally ductile, but if required in the form of wire it can be rendered ductile and fibrous by "swaging"—the process being similar to that which will be described in the case of tungsten.

Molybdenum has been proposed as a material for the filaments of electric lamps, but, as it is less refractory than tungsten, it appears to be less suitable. It is, however, adapted for the manufacture of the wire supports for tungsten filaments, and is extensively used for that purpose; it is employed also in the Coolidge X-ray tube. Molybdenum has been used as a substitute for platinum in electrical contact-breakers.

Of the compounds, ammonium molybdate has a technical importance, being used in the dyeing of silk. It has been recommended as a disinfectant for treatment of the cloth of railway carriages.

TUNGSTEN

Atomic weight 184·0

The Metal

Tungsten resembles, on the whole, chromium and molybdenum; it is an extremely hard substance, having a grey colour and bright metallic lustre. It has the highest melting-point of all metals (3,267° ± 30° C.)[1] and is extremely heavy, the specific gravity being 19·1. In its ordinary form tungsten is extremely brittle; the grains composing a piece of tungsten readily part company with one another, and intergranular fracture results. It can, however, be converted to a ductile, fibrous form by a type of mechanical work, known as "swaging." The fact that mechanical working renders tungsten more ductile appears, at first sight, contrary to the usual rule that mechanical work renders a metal harder and less ductile. The theory of swaging will be considered further in the technical section.

Tungsten crystallizes in the cubic system, the atoms being arranged—according to the results of X-ray investigation—on a centred-cube space-lattice.[2]

Compact tungsten is permanent in air at ordinary temperature and is only superficially oxidized when heated. It is unattacked by dilute sulphuric or hydrochloric acid at ordinary temperatures, but is quickly dissolved by a mixture of hydrofluoric and nitric acids, nitric oxide being evolved, and tungsten trioxide being produced.[3] It is slowly attacked by fused caustic potash.

The anodic behaviour of tungsten[4] recalls that of molybdenum. In a solution made alkaline with sodium hydroxide or even with ammonia, the anode is attacked readily enough at low current densities, soluble tungstates being produced; but it becomes passive if the current density exceeds a certain value. The passivity quickly disappears, however, if the current is shut off.

In acid solutions, on the other hand, tungsten anodes become passive much more readily. An anodically polarized tungsten anode shows a series of interesting colour changes; the order of the colours which appear upon the anode surface with increasing polarization are independent of the nature of the bath used, and have been attributed to the formation of a film consisting of definite oxides on the surface, as follows:—

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[1] I. Langmuir, *J. Franklin Inst.* **180** (1915), 490.

[2] P. Debye, *Phys. Zeitsch.* **18** (1917), 483.

[3] W. E. Ruder, *J. Amer. Chem. Soc.* **34** (1912), 387.

[4] W. E. Koerner, *Trans. Amer. Electrochem. Soc.* **31** (1917), 221.

Brown . .	attributed to WO_2
Purple . .	attributed to mixtures of WO_2 and W_2O_5
Blue . .	attributed to W_2O_5 or W_3O_8
Green . .	attributed to mixtures of W_2O_5, etc., and WO_3
Yellow . .	attributed to WO_3

There is no doubt that the yellow colour produced upon a fully polarized tungsten anode is due to the trioxide, WO_3, but the assigning of the earlier colours to definite oxides is a matter concerning which there is less certainty. If the current density exceeds 2 amps. per sq. decimetre, the anode becomes yellow almost at once. The passivated anode becomes active when allowed to stand in distilled water for some hours; a solution of sodium hydroxide renders it active almost immediately, owing to the formation of a soluble tungstate.

Laboratory Preparation. Certain technical experimenters claim to have deposited tungsten electrolytically from the solutions of the salts, but appear to have mistaken one of the lower oxides (WO) for the metal.[1] The failure of all attempts to deposit tungsten electrolytically seems to be due to the feebly basic character of the oxides. The tungsten salts are almost completely hydrolyzed, and tungsten cations can only exist in appreciable amount in the presence of a high concentration of acid; in such strongly acid solution, the whole of the current passing is devoted to the production of hydrogen, and no deposition of tungsten on the cathode is obtained.

The laboratory preparation of pure tungsten is not easy. The product obtained by heating the oxide with carbon in an electric furnace usually contains carbon, which materially alters the properties of the metal, increasing the hardness and brittleness. A purer metal is obtained by heating the trioxide in a current of hydrogen[2]; the oxides W_2O_5 and WO_2 are formed in turn and finally tungsten metal is obtained, but it is difficult to remove the last traces of oxygen. The finely divided tungsten thus prepared can be melted electrically *in vacuo* in a special apparatus, and thus brought to a compact form.[3] During the fusion, most of the impurities are eliminated by volatilization.

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[1] Compare A. Fischer, *Zeitsch. Anorg. Chem.* 81 (1913), 198.

[2] Equilibrium diagrams showing the conditions of equilibrium between the different oxides and metallic tungsten in presence of hydrogen and water vapour are given by J. A. M. von Liempt, *Zeitsch. Anorg. Chem.* 120 (1922), 267.

[3] A. Fischer and A. Roderburg, *Zeitsch. Anorg. Chem.* 81 (1913), 178.

Compounds

As in the case of molybdenum, nearly all the stable compounds are derived from the trioxide, WO_3, which has primarily an acidic character. A lower oxide, WO_2, is known with some derivatives, and many bodies known as "tungsten bronzes" can be prepared, which represent an intermediate state of oxidation. There are four chlorides, WCl_6, WCl_5, WCl_4 and WCl_2.

A. Compounds of Hexavalent Tungsten.

The **trioxide,** WO_3, is formed when either the finely-divided metal or the lower oxide is heated in air. It is a yellow substance, the colour—as is so often the case—becoming deeper, when the oxide is heated. An insoluble yellow hydrate, known as **tungstic acid,** H_2WO_4, is produced when a hot solution of a tungstate is decomposed with an acid; but, if the precipitation occurs in a cold solution, a white amorphous form containing more water is obtained; this is converted to the yellow form on boiling with water. If the addition of hydrochloric acid is made to a very dilute solution of sodium tungstate, no precipitate is produced; after removing the sodium chloride by dialysis, a quite stable colloidal solution of tungstic acid is left, which, like that of molybdic acid, can be concentrated without flocculation until a gummy residue is obtained; this gummy residue yields the anhydrous oxide (WO_3) on ignition.

The **tungstates** are formed by the treatment of the trioxide with alkalis, either in the fused state or in aqueous solution. Many series of tungstates are known, in which the proportions of basic and acidic oxides vary considerably. **Sodium normal tungstate,** $Na_2WO_4.2H_2O$, can be obtained from solutions containing excess of alkali. But if the boiling solution is made nearly neutral with hydrochloric acid, or by bubbling carbon dioxide gas through it, the salt which crystallizes out on cooling contains more WO_3; it is known as **common sodium tungstate,** $Na_{10}W_{12}O_{41}.28H_2O$, or $5Na_2O.12WO_3.28H_2O$, and forms colourless monoclinic prisms. Owing to the ease with which this salt crystallizes out, it can readily be purified, and is therefore a good material with which to start in the preparation of other tungsten compounds. The insoluble tungstates, such as **calcium tungstate,** can be formed by precipitation.

Tungsten trioxide has the property possessed by molybdenum trioxide of combining with orthophosphates to form addition products. When sodium hydrogen phosphate (Na_2HPO_4) is treated with sodium tungstate in the presence of acid, the yellow phosphotungstate, $Na_2HPO_4.12WO_3.xH_2O$, is obtained. If less acid be present, the white salt $Na_3PO_4.12WO_3.xH_2O$ separates.

Tungsten trioxide seems to have practically no basic character; it is almost insoluble in acids, except hydrofluoric acid. If tungstic acid is dissolved in hydrofluoric acid and potassium hydroxide is added, various double fluorides, such as $2KF.WO_2F_2.H_2O$, can be obtained upon crystallization.

A **trisulphide,** WS_3, is known, and is best obtained by passing hydrogen sulphide through a solution of ammonium tungstate and acidifying the solution obtained; it is a brown precipitate, but appears black when dry. It is soluble in ammonium sulphide, and from the solution red crystals of **ammonium thiotungstate,** $(NH_4)_2WS_4$, can be isolated.

B. Intermediate Oxides and their Derivatives.

It will be remembered that the partial reduction of molybdenum trioxide and its salts yields various blue products. In the case of tungsten similar intermediate bodies, many of which have a blue colour, are known. On reducing the trioxide in hydrogen at 250–300° C., a blue oxide, apparently of rather variable composition, is obtained; some authorities state it to be W_2O_5, others W_3O_8. It can, of course, be regarded as tungsten tungstate $WO_2.nWO_3$.

Especially interesting are the substances obtained by the partial reduction of the tungstates; these usually possess a bronze-like superficial lustre; hence the name, **tungsten-bronzes.** Tin, zinc, iron and hydrogen have all been used as reducing agents, whilst some experimenters recommend the electrolytic reduction of fused sodium tungstate. At least three different bronzes, differing in colour, are known; often reduction may give rise to a mixture of these compounds. If a fused mixture of sodium tungstate and a small amount of tungsten trioxide is reduced with tin, cubic crystals of a yellow bronze are obtained; if rather more tungsten trioxide is present, the product is a red bronze, to which the formula $Na_2W_3O_9$ has been ascribed, whilst from still more acid mixtures a blue bronze, said to be $Na_2W_5O_{15}$, appears.[1] All these formulæ should be accepted with caution.

When acidified solutions of tungsten trioxide are treated with zinc or tin, a blue solution is produced, which—arguing by analogy from the case of molybdenum—contains the colloidal oxide W_3O_8. If the reduction is continued, however, further colour changes are seen. A solution of potassium tungstate containing oxalic acid when reduced with tin becomes first blue, then green, and finally deep red. From the red solution a double oxalate of pentavalent tungsten having the composition $3K_2O.2W_2O_5.4C_2O_3.9H_2O$ has been isolated as a red crystalline powder. The details of the preparation and purification—which presents considerable difficulty—must be sought elsewhere.[1]

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[1] J. Philipp, *Ber.* 15 (1882), 499. Compare E. Schaefer, *Zeitsch. Anorg. Chem.* 38 (1904), 142.

C. Compounds of Tetravalent Tungsten.

When the trioxide is reduced with zinc in the presence of a little hydrochloric acid, the **dioxide,** WO_2, is formed as a brown powder. If much acid is present, the oxide, which has a basic character, dissolves, yielding a purple solution containing a salt. The salts are, however, difficult to isolate from such solutions in the solid form. Both salt solutions and oxide are readily oxidized by the air. The dioxide has little acidic character; if treated with alkali, it evolves hydrogen and forms a tungstate. The **sulphide,** WS_2, corresponding to it can be obtained by heating the **trisulphide** (WS_3).

D. Highly Oxidized Compounds of Tungsten.

By adding hydrogen peroxide to a solution of sodium tungstate, a yellow coloration is produced, and by crystallization *in vacuo*, **sodium pertungstate,** $NaWO_4.H_2O$, is deposited.

E. Miscellaneous Compounds.

Chlorides. As in many previous cases, the various chlorides are difficult to isolate from the solutions of the oxides in hydrochloric acid, and must be prepared in a dry way. Four chlorides exist. The **hexachloride,** WCl_6, is formed by the action of dry chlorine in excess upon heated tungsten. If moisture or oxygen is present an oxychloride is also formed. The hexachloride is a violet crystalline substance, melting at 275° C., and boiling about 350° C. At low temperatures the vapour density is normal, indicating that the molecule is WCl_6; at higher temperatures, the density becomes abnormally low—a fact pointing to dissociation into a lower chloride and free chlorine. The presence of moisture causes hydrolysis to oxychlorides such as $WOCl_4$ and WO_2Cl_2, with evolution of fumes of hydrogen chloride, whilst excess of water causes complete hydrolysis to the oxide WO_3 or a hydrate; curiously enough, neither of the hydrolytic changes commence at ordinary temperatures, unless a trace of an oxychloride is already present.

If a slow stream of hydrogen is passed over the hexachloride below its boiling-point, the **pentachloride,** WCl_5, is formed, and may be condensed in a cool receiver. The product is, however, impure, and should be redistilled in a current of carbon dioxide, a residue of the less volatile tetrachloride being then left behind. The pentachloride is dark green, and when treated with water, yields a green solution which hydrolyses, gradually depositing a blue intermediate oxide. The **tetrachloride**, WCl_4, is brown, and, unlike most tetrachlorides, scarcely volatile; in the presence of water, it suffers hydrolysis, yielding the brown oxide WO_2.

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[1] Q. O. Collenberg, *Zeitsch. Anorg. Chem.* **102** (1918), 247. Some other pentavalent tungsten compounds are described by A. Fischer and L. Michiels, *Zeitsch. Anorg. Chem.* **81** (1913), 102.

If the reduction of the hexachloride in hydrogen is conducted at still higher temperatures, the grey **dichloride**, WCl_2, which is also non-volatile, is produced; this chloride evolves hydrogen when treated with water. It is possible to carry the reduction even further, and to obtain metallic tungsten by heating the lower chlorides in hydrogen at a very high temperature.

Although the simple **trichloride** (WCl_3) is not known, yet double chlorides, such as $2WCl_3.3KCl$, have been prepared.[1] A solution of potassium tungstate is added in small quantities to excess of boiling hydrochloric acid, which is then quickly cooled (under these conditions, tungstic acid is not precipitated to any considerable extent). The solution is reduced with tin at 40–60° C., the colour becoming first blue, then violet, then reddish brown, and finally a dark green-yellow; the last-named colour indicates the trivalent state. The liquid is now treated with hydrogen chloride gas and cooled in a mixture of ice and salt; a crystalline powder, of colour varying from yellowish green to yellowish brown, is then deposited, which has the composition indicated above.

Carbides.[2] It has already been stated that the presence of carbon in tungsten increases the hardness. Two carbides of tungsten, W_2C and WC, have been described, being obtained by heating carbon with tungsten and tungsten oxide respectively; they are very hard, grey substances. The carbide WC is best known, however, as a constituent of tungsten steel.

Analytical

The reactions of tungsten compounds are very similar to those of molybdenum. Neutral solutions of soluble tungstates yield white precipitates with salts of lead or mercury. When treated with hydrochloric acid, they yield a precipitate of tungstic acid. If the solution is hot the precipitate is yellow, and insoluble in dilute acids. If the solution is cold, the precipitate is white;

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[1] O. Olsson, *Ber.* **46** (1913), 566.

[2] H. Moissan, *Comptes Rend.* **123** (1896), 13; P. Williams, *Comptes Rend.* **126** (1898), 1722; J. O. Arnold and F. Ibbotson, *J. Iron Steel Inst.* **99** (1919), 407.

addition of metallic zinc to the acidified solution causes a blue colour. If a neutral solution of a tungstate is treated with ammonium sulphide, followed by an acid, a pale brown precipitate of the sulphide, soluble in ammonium sulphide, is produced.

The method of separation of tungsten from other metals is the same as that of molybdenum; the quantitative separation of these two metals, which are so similar, is a troublesome operation. One of the methods available has been indicated in connection with the estimation of molybdenum; it depends on the fact that the trioxide of tungsten is less soluble in sulphuric acid than that of molybdenum. Having separated the molybdenum, the tungsten is converted to the state of trioxide (WO_3), which is ignited and weighed.

TERRESTRIAL OCCURRENCE[1]

Tungsten is one of the elements which become concentrated in the last solidifying portion of an igneous rock-magma, and tungsten compounds are found, principally, in the quartz-veins associated with granitic intrusions. The commonest mineral is a tungstate of iron, usually containing manganese also, known as

Wolfram . . $(Fe,Mn)WO_4$.

Wolfram is often found closely associated with tin ores, and sometimes with minerals like tourmaline; this fact suggests that tungsten, like tin, may have been given off, in the final stage of the consolidation of the igneous magma, in the vaporous state. Wolfram is found, for instance, along with cassiterite, in the rock known as greissen, which is a granite altered through the agency of vapours. Many tin ores, including those of Cornwall, contain a considerable amount of tungsten.

Wolfram is a heavy, blackish, opaque mineral; it is usually found in columnar form, or as granules, and is generally embedded in other minerals (e.g. quartz); well-formed crystals are rare.

The most important deposits of tungsten are found at points situated on a circle round the Pacific Ocean. New South Wales, Queensland, the Malay States, Lower Burma, China, Japan, Alaska, California, Nevada, Colorado, Mexico, Bolivia and Peru are—or have been—producers of tungsten. Perhaps the most important locality is the Tavoy district of Burma, where quartz veins occur containing wolfram, associated with molybdenite, columbite, tourmaline, and often cassiterite; the veins are connected with a granite intrusion of an exceptionally acid type. The

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[1] F. J. Johnstone, *J. Soc. Chem. Ind.* **37** (1918), 294R; C. G. Fink, *Min. Ind.* **28** (1920), 688. See also *Engineering*, **99** (1915), 412; J. M. Campbell, *Econ. Geol.* **15** (1920), 535.

Australian and United States ores are also important. Along with wolfram, there occur—especially in America—other tungstates, such as

Scheelite . . .	$CaWO_4$
Hübnerite . . .	$MnWO_4$
Ferberite . . .	$2(Fe,Mn)WO_4.(Fe,Mn)O$

Outside the Pacific ore-circle rich ores of tungsten occur in Portugal in quartz veins springing from granite, and in the detrital matter covering the hills derived from these veins. Here again tin occurs with tungsten.

Wolfram is a mineral easily attacked by weathering agencies, and alteration products, such as

Tungsten ochre . . . WO_3,

are often met with.

TECHNOLOGY OF TUNGSTEN

Concentration.[1] The tungsten ore as it is mined requires concentration before being exported, since the wolfram comes up diluted with much quartz and other gangue material. The wolfram can largely be separated from the quartz and other light minerals owing to the difference in **gravity**. The ore is crushed, and concentrated on tables, similar to the Wilfley table described in the Introduction (Vol. I, page 123). The heavy particles, including wolfram and other tungstates, are caught behind the riffles, and are shaken off at the end of the table, whilst the lighter siliceous material is washed over the riffles and passes out separately.

A good deal of the more finely powdered matter which is necessarily produced during crushing cannot economically be treated on tables, as the finer wolfram particles would be carried over the riffles. Such material (the "slimes") requires special treatment, usually on a vanner (see Vol I, page 121). In one form of vanner used for the concentration of tungsten ore the ore-pulp is fed on to the travelling belt at one side; the siliceous matter is washed right across the belt, and falls over the other side, whilst the heavier tungstate particles sink sufficiently to adhere to the belt, and are carried along with it and fall off at the end. As a rule, the whole machine is given a longitudinal shaking motion.

No gravity process, however, is able to separate wolfram from the other heavy minerals, notably cassiterite, which may be present, and it is usual to complete the concentration by a **magnetic** process, advantage being taken of the fact that the tungsten mineral is slightly magnetic. The principles of magnetic separation have also been discussed in the Introduction (Vol. I, p. 126).

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[1] H. C. Parmalee, *Met. Chem. Eng.* 9 (1911), 341, 409; G. W. Wepfer, *Eng. Min. J.* 97 (1914), 1251.

In addition to the wolfram concentrates obtained from tungsten ores proper, concentrates are obtained as bye-products from the dressing of tin ores. In the United States, ferberite and scheelite ores are treated in many districts, whilst hübnerite is an important mineral both in that country and in Bolivia.

Manufacture of Tungsten Trioxide.[1] The comparatively rich concentrate consisting, in most cases, mainly of wolfram, can then be shipped or sent by rail to the industrial district where it is to be worked up. A considerable development of the tungsten industry in this country, chiefly at Widnes and Luton, occurred during the war, but the exceptional demand for tungsten has now ceased. The United States and Germany have, for some time, been large producers of tungsten.

The concentrate is ground up with sodium carbonate, and the mixture is heated in small basic-lined reverberatory furnaces at 800–1,100° C. for some hours, the charge being continually rabbled. The temperature must be sufficient to render the mass pasty, but not to cause complete fusion. An oxidizing atmosphere should be maintained in the furnace. During the process, sodium tungstate is produced in the mass, the iron and manganese being respectively oxidized to the oxides Fe_2O_3 and MnO_2 (or perhaps Mn_3O_4). The product is tapped in a pasty condition and, when cool, it is ground, and the sodium tungstate is extracted with water. The solution of sodium tungstate is then treated with hydrochloric acid which precipitates the yellow tungstic acid; by redissolving the yellow precipitate in ammonia and once more precipitating with acid, a considerable amount of purification can be effected. Finally by calcining the precipitate, tungsten trioxide (WO_3) is obtained.

In one variation of the process, the sodium tungstate solution obtained by leaching is treated with calcium chloride solution. Calcium tungstate is thus precipitated and is afterwards converted to tungstic acid by the action of an acid.

Ferro-tungsten and Tungsten Steel. From tungsten oxide the different technically useful compounds of tungsten can be obtained. **Ferro-tungsten,** made by reducing a mixture of tungsten and iron oxides with carbon in an electric furnace, will be considered more fully in the section on ferro-alloys. Instead of a mixture of oxides, the mineral ferberite, which is a natural iron tungstate, is often used. Ferro-tungsten is largely used in the manufacture of **tungsten steel**, a material employed very generally in the making of high-speed tools, which are liable during their use to become heated to temperatures at which ordinary steels would lose their hardness. In recent years, however, the introduction of high-grade metallic tungsten powder as a comparatively cheap commercial product has caused many steel-makers to employ this material in the place of ferro-tungsten in the manufacture of tungsten steel.[1] It is made by reduction of the oxide in hydrogen at a high temperature, and contains 98–99 per cent. of tungsten.[2]

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[1] See *Engineering*, **104** (1917), 432. See also C. H. Jones, *Met. Chem. Eng.* **22** (1920), 9. A French process is described by C. Matignon, *Chim. et Ind.* **3** (1920), 277, 422.

Many of the steels used for the manufacture of permanent magnets contain tungsten.

Manufacture of Electric Lamp Filaments.[3] One of the most important uses of tungsten—its employment in the form of a thin filament in the electric vacuum lamp—depends on the extremely high melting-point of the metal, and its comparative non-volatility at high temperatures. In the manufacture of tungsten filaments, the powdered trioxide is usually moistened with a small quantity of thorium nitrate solution and then dried and ignited at 1,100° C. for about an hour in a fire-clay crucible; during this "firing" the small grains of the oxide unite to form larger grains. The amount of thorium salt added must be enough to make 0·75 per cent. of thorium oxide in the product; the function of the thorium oxide will be discussed later. Some filaments contain no thoria.

The fired oxide is then **reduced** to the metallic state by heating in hydrogen at 1,000° C. in an electrode furnace consisting of a silica tube wound with nichrome wire. The product is metallic tungsten (still containing thorium oxide) in coarse powder.

The powder can be pressed dry into a rod, but the rod is so fragile that it cannot be lifted. It must, therefore, be "slid" into position in an electric furnace where it is "baked" in hydrogen at 1,250° C. The baking renders the rod less fragile, although it is still porous. It can now be clamped at the two ends by two electrodes connected to a source of current and heated by the direct passage of electricity to 3,000° C. in an atmosphere of hydrogen; the operation, which is known as "sintering," renders the rod non-porous.

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[1] See, however, J. W. Weitzenkorn, *Met. Chem. Eng.* 26 (1922), 504, who thinks the use of ferro-tungsten gives a more uniform steel than tungsten powder; the pure tungsten owing to its high melting-point is liable to remain undissolved by the steel, and to collect at the bottom of the crucible as a segregation.

[2] J. L. F. Vogel, *J. Soc. Chem. Ind.* 39 (1920), 103R.

[3] Z. Jeffries, *Bull. Amer. Inst. Min. Eng.* 138 (1918), 1037; C. H. Desch, *Engineering*, 110 (1920), 416; W. D. Coolidge, *Engineering*, 110 (1920), 109; C. H. Jones, *Met. Chem. Eng.* 22 (1920), 9; H. Jennicke, *Chem. Zeit.* 38 (1914), 631; "A. D.," *Met. u. Erz.* 17 (1920), 449.

The compact tungsten obtained in this way is still non-ductile, and would break at once if any attempt were made to draw it into wire in the ordinary way. It must be converted to the fibrous ductile form by a process of swaging. The swaging machine is an adaption of a machine long used in the manufacture of steel needle blanks[1] (see Fig. 18). A split die, D_1D_2, of suitable size is attached to an axle J, which can be made to rotate at about 600 revolutions a minute within a stationary shell fitted with about ten rollers, R. Each time a roller is passed the half-dies are forced together, and thus a rod of tungsten placed at J in the jaws of the machine receives about 6,000 impacts per minute. Before being placed in the machine the rod is heated in an electric furnace, and then brought by means of tongs between the jaws. At the start the rod is square, but the repeated impacts render it round, and, at the same time, rather thinner and slightly longer. When the diameter is reduced by about 10 per cent. the rod is reheated in the electric furnace, and swaged between half-dies of slightly smaller diameter. Thus starting with a square rod of diameter of about 2 centimetres, the diameter can be gradually diminished, and the length correspondingly increased until a thin round rod of diameter of 0·76 mm. is arrived at. The temperature of swaging should be 1,600–1,700° C. at the commencement of the process, but is gradually reduced to 1,300° C. as the deformation increases.

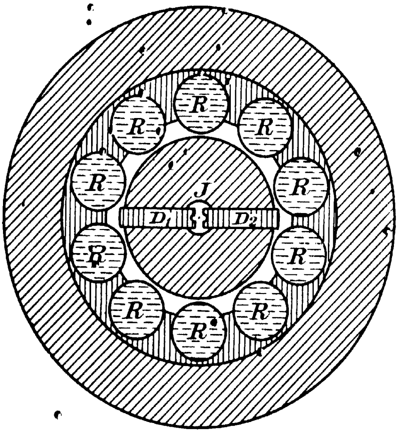

Fig. 18.—Swaging Machine.

As the swaging proceeds, the rod becomes less fragile, and the tensile strength greatly increases; when the diameter has reached 0·8 mm. the tungsten has become ductile, and it can then be drawn out into still thinner filaments by the normal process of wire-drawing, diamond dies being usually employed. In this way filaments of the diameter required for use in the lamps are obtained.

The theory of swaging is extremely interesting. The structure of the original tungsten rod has been studied by means of micro-sections, and is seen to consist of ordinary equiaxed polygonal grains, similar to those of any ordinary cast metal, such as copper or iron, which has been allowed to solidify slowly. The apparent brittleness of tungsten is due to the fact that the boundaries of the grains are not surfaces of strength—as in the case of most metals—but surfaces of weakness. The smallest force is sufficient to cause the grains to part from one another, and inter-granular fracture is the result; within a single crystal, there is no special tendency towards fracture.

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[1] Described in U.S. Patents 268874 (1882), 376144 (1888), and 515576 (1894). See also N. L. Müller, *Zeitsch. Angew. Chem.* 26 (1913), i. 404 422.

The inter-granular fragility is generally thought to be a specific property of pure tungsten.[1] It may conceivably be due, however, to the presence of a network of impurities separating the grains, such as is known to be the cause of inter-granular fragility in copper containing bismuth.[2] Or again, it may be due to the unusual method by which the tungsten rod is produced—by sintering instead of by fusion. Whichever explanation is correct, it is certain that, if the grain-boundaries can be arranged in a direction along which fracture is inherently improbable, the special fragility of tungsten can be avoided.

This is accomplished by the process of swaging. The grains of the metal become elongated in the direction of the length, and reduced in the direction at right angles. By the time the rod has been squeezed out into wire of diameter 0·007 inch each of the original grains has become a fibre perhaps an inch long, and about 0·00002 inch in diameter. Thus the structure of swaged tungsten is fibrous. All the surfaces of the weakness are parallel to the length of the filament; there is no inter-granular boundary at right angles to the length which might allow of fracture.

That this explanation is correct is shown by fact that if a swaged tungsten rod be placed on an anvil and struck with a hammer, it will often split lengthwise into a number of thinner parallel fibres. Evidently the surfaces of weakness are still there, but they are disposed in such a way as to be—to all intents and purposes—harmless.

Although the tungsten filament is fibrous at the moment of manufacture, considerable changes in the structure may occur when the lamp is used. At the temperature reached during burning, rapid crystal growth occurs in a tungsten filament free from thoria; after "burning" for a short time, perhaps about fifteen minutes, the crystals have grown to a large size, single crystal boundaries often extending right across the filament, a condition which clearly renders the filament weak; after this no further increase of the average grain-size occurs, but the boundaries seem to keep shifting as burning proceeds, and this shifting is accompanied by deformation of the filament, which may ultimately lead to fracture. The function of the thorium oxide is to restrict the growth of the tungsten grains during burning, and thus to prolong the life of the filament.[1] It does not prevent the conversion of the original fibrous structure to an equiaxed structure, but a filament containing thoria remains fine-grained even when burnt for a very long period. The thoria segregates at the boundaries between the grains when the filament is heated, and prevents the exaggerated grain-growth which would cause weakness. Other impurities, like lime and alumina, which are insoluble in tungsten, likewise tend to segregate at the grain-boundaries and to prevent the form of grain-growth which is characteristic of pure tungsten; on the other hand, impurities which are soluble in tungsten (e.g. tungsten bronzes) have no obstructive influence on grain-growth, but rather seem to favour the exaggerated growth of certain crystals.

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[1] C. G. Fink, *Met. Chem. Eng.* 8 (1910), 340.

[2] J. C. W. Humphrey, *Bull. Amer. Inst. Min. Eng.* 130 (1916), 1040.

It is noteworthy that filaments fail much more quickly when alternating current is used for lighting than when direct current is employed. The different crystals composing the filament tend to slide over one another along the crystal-boundaries when alternating current passes, so that the filament—originally straight—acquires a zigzag outline. This phenomenon, which is known as "offsetting," has been ascribed to the trembling of the filament produced by the passage of alternating current. Owing to the increasing use of alternating current for lighting purposes, the matter is of some importance, and much work has been devoted to produce a filament stable towards alternating current; it is claimed that by the introduction of lime—or of a trace of phosphorus—into the filament, the trouble can to a great extent be overcome.

Although thoria reduces the tendency to recrystallize, it does not entirely prevent it. If we can produce a filament consisting of a single long thin crystal-grain, inter-granular fracture will clearly be impossible, and this particular cause of failure will be eliminated. A recent German process[2] aims at the manufacture of such filaments. In this process a tungsten-filament containing thorium is made by "squirting" a plastic mixture containing a binder through an orifice, and the filament thus produced is passed continuously through a zone surrounded by an electrically heated coil at the rate of about 2½ metres per hour. The temperature of the zone is about 2,400–2,600° C., and a hydrogen atmosphere is employed. At that temperature, the recrystallization velocity of tungsten exceeds the velocity with which the filament passes through the zone, and the filament comes out of the zone with all the atoms arranged according to a single orientation. That is to say, the whole filament consists of a single crystal. It is cut into the lengths required and fitted in lamps without further treatment. It will be interesting to see how the life of these lamps compares with those of ordinary drawn tungsten filaments. The inventors claim that the filament is unchanged by burning.

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[1] C. J. Smithells, *Trans. Faraday Soc.* **17** (1922), 485; *J. Inst. Met.* **27** (1922), 107.

[2] F. Schöter, *J. Gasbeleuchtung*, 61 (1918), 44.

Although to the ordinary observer the single-crystal filament does not appear different to the common filament of fibrous tungsten, yet the crystalline character may be shown by etching. The etched filament has an octagonal cross-section, and, if slowly rotated in light coming from a single source, and carefully watched, it will be seen to "flash out" brightly eight times each revolution, whenever one of the eight faces happens to present such an angle to the light as to reflect it into the eyes of the observer.

Power-consumption of Electric Filament Lamps. Lamps provided with tungsten filaments are more efficient as light-producers than the old-fashioned lamps with carbon filaments, simply because tungsten can be heated up to a higher temperature than was possible in the case of carbon. As explained in the section upon the gas-mantle, of the total radiation given off by any "black" (non-transparent) body the proportion of "visible" rays increases steadily as the temperature rises. In the old carbon lamps, the filament could not safely be heated above 2,000° C., and the consumption of electric power was 3 to 4 watts per candle-power; in the ordinary tungsten lamps a temperature of about 2,130° C. is obtained, and the consumption is only about 1·1 watts per candle-power.

By applying an abnormally high E.M.F. to an ordinary tungsten lamp, and thus heating the filament to a still higher temperature, we can obtain—for a time—a still greater efficiency of light-production; but, in an ordinary evacuated lamp, the tungsten begins to volatilize quickly, as soon as the temperature exceeds the value for which the lamp was designed. The volatilized tungsten will condense on the glass and cause blackening, which interferes with the passage of the light; moreover, if the volatilization is allowed to go on, the lamp will soon "burn out."

There is, however, a class of lamps[1] now manufactured containing an inert gas such as argon or nitrogen, the presence of which, controls the tendency of the tungsten to volatilize, and allows a higher temperature to be reached safely. Such lamps are often known as "half-watt lamps," and have actually a power-consumption in some cases as low as 0·4 to 0·5 watts; the pressure of the inert gas within the lamp is usually in the neighbourhood of half an atmosphere. The design of a gas-filled lamp, however, presents special difficulties, as the presence of the gas is liable to cause removal of heat from the filament by convection-currents—a loss which cannot occur in the evacuated lamp. The special arrangement of the filament, which is often coiled into a close helix, is designed to minimize the loss through convection. The lamp must also be designed so that the convection-currents of gas charged with tungsten vapour shall strike the globe at some point at the top of the lamp through which light would not normally need to pass; thus, whatever "blackening" does occur, it will not interfere with the luminosity of the lamp. Up to the present time, half-watt lamps of low candle-power have not been introduced, although powerful lamps, suitable for outdoor use (where arc lamps were previously employed), are made in large quantities.

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[1] I. Langmuir, *Met. Chem. Eng.* **11** (1913), 613; I. Langmuir and J. A. Orange, *Met. Chem. Eng.* **11** (1913), 613.

Since the proportion of short waves in light emitted by an incandescent body increases with the temperature, the light of the half-watt lamp, in which the filament is 400–600° C. higher than that of the ordinary tungsten filament lamp, is exceptionally "white."

Other Uses of Metallic Tungsten.[1] In addition to its employment in lamps and in steel, metallic tungsten has proved useful as a substitute for platinum in electrical contacts on magneto-coils, relays and similar instruments. Although inferior to platinum as regards liability to oxidation, it is actually superior in the matter of fusibility and volatility. The good heat-conductivity of tungsten serves to prevent undue heating at the point of arcing, and no doubt this is one reason why the oxidation at a tungsten contact is not more serious. Electric furnaces consisting of alundum tubes wound with tungsten wire have proved more serviceable, as well as cheaper, than those wound with platinum. On account of its high melting-point it has proved extremely suitable, in the construction of X-ray tubes, as a material for the "target" upon which the cathode-ray particles are directed.

Uses of the Salts. Tungsten salts have found application as mordants in dyeing, and also in the process of rendering textiles fireproof. They are used in the glass and ceramic industries for the production of a yellow colour.

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[1] W. D. Coolidge, *J. Ind. Eng. Chem.* 4 (1912), 2.

URANIUM

Atomic weight . . . . 238·2

The Metal

Uranium is the last member of the group. The properties of this metal—more than those of any other—are rendered doubtful by the difficulty of isolating the element in the pure state. The purest metal yet obtained is a hard grey substance, capable of taking a lustre when polished. It is very heavy, although, curiously enough, slightly less heavy than tungsten, the specific gravity being 18·7. Uranium is by no means so infusible as tungsten, the melting-point being probably somewhat above 1,400° C.

Finely divided uranium becomes oxidized spontaneously in the air, and may even catch fire owing to the heat developed; when exposed to carbon dioxide, it becomes covered, apparently, with a thin protective oxide-film, and afterwards can be exposed to air without change. In the state of coarse powder, uranium oxidizes only when heated, and the compact metal is moderately stable in air.

Uranium is distinctly reactive, and, when in the form of powder, decomposes water; it dissolves more quickly in dilute hydrochloric or sulphuric acid, hydrogen being evolved. Uranium precipitates tin, copper, silver and gold from solutions of their salts.

The anodic behaviour [1] of uranium presents a contrast to those of the other metals of Group VIA. Uranium anodes do not readily become passive, and even when a brown layer of oxide appears on the anode surface, it does not in general appear to interfere seriously with the anodic reaction. In sulphuric, hydrochloric, or even nitric acid, the uranium is anodically dissolved, passing into the solution mainly in the tetravalent condition. On the other hand, in an alkaline bath, or a solution of a phosphate, a yellow film usually appears upon a uranium anode, which obstructs to some extent the passage of the current.

Laboratory Preparation. Metallic uranium cannot be deposited electrolytically from an aqueous solution. The reason is no doubt the same as that suggested in the case of tungsten—the almost entire absence of simple uranium cations from the solutions of the salts. The electrolysis of a uranium salt solution usually leads merely to the production of hydrogen at the cathode, often accompanied by the deposition of hydrated oxides of uranium. If, however, an aqueous solution of the tetrachloride is electrolysed with a mercury cathode, uranium amalgam is said to be obtained, the high overpotential of mercury no doubt restraining the evolution of hydrogen.[1] When the amalgam is heated *in vacuo*, the mercury is driven off, leaving uranium in a pyrophoric condition.

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[1] U. Sborgi, *Zeitsch. Elektrochem.* 19 (1913), 115.

The method is, however, by no means a convenient way of obtaining uranium, and dry methods are usually employed, based upon the reduction of the oxide with carbon, aluminium or magnesium. When carbon is used, the uranium obtained invariably contains carbon, whilst the metallic reducing agents commonly fail to remove the whole of the oxygen.

In reading statements regarding the purity of metals of high atomic weight, such as uranium, it should always be remembered that the true purity of the sample is never so great as the analytical results (expressed in the ordinary way) appear to show. For instance, owing to the unusually high atomic weight of uranium, the carbide U_2C_3 itself contains as much as 93 per cent. of uranium, with only 7 per cent. of carbon. Consequently the product obtained by the reduction of the oxide with sugar-charcoal in the electric furnace,[2] although its analysis may perhaps show only 1 per cent. of carbon, cannot rightly be regarded as containing 99 per cent. of elemental uranium. It is more correct to regard it as consisting of 93·4 per cent. of metal and 6·6 per cent. of the carbide U_2C_3.

A method based upon the reduction of the oxide U_3O_8 with magnesium vapour is capable of producing a powder which contains as much as 99·5 per cent. of uranium, with 0·5 per cent. of oxygen.[3] The procedure consists in heating a mixture of the uranium oxide (U_3O_8) and magnesium powder—pressed into the form of a solid rod. The heating is conducted in a magnesia tube, embedded in an electric resistance furnace. The temperature is first raised by passing a current through a resister of granular carbon surrounding the tube. When hot, however, the contents of the tube become conducting and are heated by direct passage of electricity through them, by means of carbon electrodes introduced at the two ends. During the whole process, a current of hydrogen is passed through the tube. When the required temperature is reached, the magnesium is in the vaporous condition and is able to reduce the uranium to the metallic state. After the operation the hydrogen is replaced by carbon dioxide, since otherwise the metal would ignite spontaneously when exposed to the air. Afterwards the finely divided uranium is washed with acetic acid, to remove magnesia. The uranium remains undissolved, each particle being covered—as has been mentioned—with a little uranium oxide. The powder can be fused and converted to compact uranium by heating in a special form of electric vacuum furnace.

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[1] J. Férée, *Bull. Soc. Chim.* 25 (1901), 622.

[2] H. Moissan, *Comptes Rend.* 122 (1896), 1088.

[3] E. K. Rideal, Dissertation, Bonn (1913), pp. 40–43. See also E. K. Rideal, *J. Soc. Chem. Ind.* 33 (1914), 673.

Uranium and all its compounds undergo spontaneously a radioactive transformation, giving rise to uranium X_1, a metal having chemical properties different from those of uranium. These changes have been discussed in Chapter XV (Vol. I).

Compounds

The important compounds of uranium are derived from two oxides, UO_3 and UO_2. The trioxide (UO_3) has a much more pronounced basic character than the trioxides of the other metals of the group, although the salts are not normal compounds of the type UX_6, but basic (*uranyl*) salts of the type $[UO_2]X_2$. The acidic character is less striking, and the salts formed with basic oxides are insoluble. The dioxide (UO_2) has a basic character. A stable intermediate oxide, U_3O_8, without derivatives, exists. A few compounds corresponding to the sesquioxide (U_2O_3) are known, and the oxide itself has been prepared in a hydrated condition. A tetroxide, UO_4, can be prepared, which has an acidic character, several "peruranates" being known.

When uranium or any of its oxides is heated in air above 600° C., it is the intermediate oxide (U_3O_8) which is formed. This stable oxide yields the dioxide UO_2 when heated in hydrogen. When dissolved in sulphuric or hydrochloric acid, the oxide U_3O_8 yields a mixture of the salts of UO_2 and UO_3. If, however, it is dissolved in nitric acid, it is converted entirely to uranyl nitrate $[UO_2](NO_3)_2$, and the latter yields the trioxide UO_3 on gentle ignition below 400° C.

A. Compounds of Hexavalent Uranium (Uranic and Uranyl Compounds).

Uranium trioxide, UO_3, is formed, as has just been explained, when uranyl nitrate is heated in the air below 400° C. It is an orange substance in the anhydrous condition; the hydrate, $UO_3.2H_2O$, is obtained when the heating of the nitrate is very gentle, or when an alcoholic solution of uranyl nitrate is evaporated to dryness. The anhydrous trioxide is stable in air below 400° C.; above 500–600° C. it commences to lose oxygen, yielding the intermediate oxide (U_3O_8).

The trioxide has a distinct basic character. It dissolves in acids yielding green-yellow solutions. These solutions deposit on concentration yellow crystalline salts, which, as already stated, are not normal salts, but basic salts, like **uranyl nitrate,** $[UO_2](NO_3)_2.6H_2O$, **uranyl sulphate** $[UO_2]SO_4.3H_2O$, and **uranyl chloride,** $[UO_2]Cl_2.H_2O$, derived as though from the divalent radicle $(UO_2)^{\cdot\cdot}$ which is known as *uranyl.* The hexavalent ion $U^{\cdot\cdot\cdot\cdot\cdot\cdot}$ does not seem to have any real existence in the solution, and the salts are usually regarded as being ionized thus :—

$$[UO_2]SO_4 \rightleftharpoons [UO_2]^{\cdot\cdot} + (SO_4)''.$$

There is, however, some hydrolysis, and for the most part the solutions of the salts are acid to litmus. When boiled they yield more basic salts; a solution of uranyl sulphate (UO_2SO_4 or $UO_3.SO_3$), for instance, after boiling deposits crystals of $4UO_3.SO_3$. Uranyl salts, both in the solid state and in solution, show a very characteristic yellow-green fluorescence, the cause of which will be discussed later.

The insoluble uranyl salts are formed by precipitation. The **phosphate** $(UO_2)HPO_4$ is obtained as a pale yellow precipitate when a solution of sodium phosphate is added to a solution of a uranyl salt containing acetic acid; if ammonium salts are present in large quantities, the double salt $NH_4(UO_2)PO_4$ is obtained. Both precipitates are remarkably insoluble in water and in acetic acid, but are dissolved by hydrochloric acid. The **ferrocyanide** is a reddish-brown precipitate formed on the addition of potassium ferrocyanide to a uranyl salt.

Uranium trioxide has also an acidic character, but the **uranates** are insoluble in water. As a result, they are produced, instead of the hydrated trioxide, when the uranyl salts are precipitated with alkalis. For instance, when a solution of uranyl nitrate is treated with caustic potash, **potassium diuranate,** $K_2U_2O_7$, is thrown down as a yellow precipitate; the sodium and ammonium diuranates are obtained in a similar way.

Normal uranates (K_2UO_4) as well as the triuranates ($K_2U_3O_{10}$), tetra-uranates ($K_2U_4O_{13}$) and hexa-uranates ($K_2U_6O_{19}$) are known, but they are all insoluble.

B. Intermediate Oxides of Uranium.

When the trioxide is heated above 500–600° C. in air, it loses oxygen and becomes converted to a greenish-black substance. If the trioxide is in a fine state of division, and the heating is not accomplished at too high a temperature, preferably being completed in an atmosphere of oxygen, the composition approximates closely to U_3O_8. If the temperature employed is very high, more oxygen is given up, and the composition may come nearer to that expressed by the formula U_2O_5. Many chemists regard U_3O_8 as uranous uranate $UO_2.2UO_3$.

A hydrated form[1] of U_3O_8 is produced when an aqueous solution of uranyl acetate containing ether suffers spontaneous reduction by exposure to light, and when uranous hydroxide is allowed to oxidize in the air; prepared in the first way it appears as a flocculent violet precipitate, while the second method yields a very dark green product.

C. Compounds of Tetravalent Uranium (Uranous Compounds).

The **dioxide**, UO_2, is obtained when the trioxide (UO_3) or inter mediate oxide (U_3O_8) is reduced by heating in hydrogen. It is a heavy substance varying in colour from red-brown to black according to the conditions of preparation. When exposed to the air, it readily becomes oxidized to U_3O_8. The hydroxide, obtained by precipitation of a uranous salt with an alkali, has a red-brown colour.

Uranous oxide has a distinct basic character, and dissolves in acids, yielding deep-green solutions, from which the **uranous salts** can be isolated. The uranous salts can also be prepared by reducing an acidified solution of a uranyl salt with zinc, or, in the presence of light, with alcohol. For instance, if a solution of uranyl sulphate, $[UO_2]SO_4$, is treated with alcohol and sulphuric acid and exposed to sunlight, the yellow colour changes to green, and from the green solution, **uranous sulphate**, $U(SO_4)_2.8H_2O$, can be obtained in green crystals; various other hydrates are known. The corresponding **chloride**, UCl_4, although more usually prepared by a dry method, can be obtained in a similar way. An alcoholic uranyl chloride solution containing hydrochloric acid is exposed to the sunlight, and the uranous chloride produced is precipitated by adding ether. Uranous salts are strong reducing agents.

The insoluble uranous salts are obtained as usual. The **sulphide**, US_2, is a black compound precipitated when ammonium sulphide is added to a uranous salt solution, while the **phosphate** is a green, gelatinous precipitate.

D. Compounds of Trivalent Uranium.

The **trichloride**, UCl_3, can be obtained by heating the tetrachloride, UCl_4, in a current of hydrogen, or alternatively by the prolonged reduction of a uranyl chloride solution with zinc and hydrochloric acid. The reddish solution is somewhat unstable—gradually evolving hydrogen and assuming the green colour characteristic of uranous salts. But if—before this occurs—the reddish solution is treated with potash, an unstable brown **hydroxide,** $U(OH)_3$, is produced. This is very fugitive and even in the absence of air passes to uranous hydroxide, hydrogen gas being evolved.

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[1] J. Aloy, *Bull. Soc. Chim.* **23** (1900), 368.

E. Highly Oxidized Compounds of Uranium.

When hydrogen peroxide is added to a solution of a uranyl salt (e.g. the nitrate), a **tetroxide,** UO_4, which has no basic properties, is thrown down in a hydrated condition as a yellow precipitate; it is impossible to drive off the whole of the water without causing loss of oxygen.[1] A **potassium peruranate,** derived from the same oxide, is formed by adding alcohol and then potassium hydroxide; it is a red substance with the composition $K_2UO_5.3H_2O$. But, when aqueous hydrogen peroxide acts upon a uranyl nitrate solution in the presence of considerable excess of potassium hydroxide, a bright yellow solution is produced, which yields, on precipitation with alcohol, a yellow salt containing still more oxygen. This has the composition, $2K_2O_2.UO_4.10H_2O$, and is usually regarded as a compound of uranium tetroxide and potassium peroxide. Sodium and ammonium salts are obtained in analogous ways, whilst insoluble peruranates, such as the calcium salt, can be prepared by precipitation.

F. Miscellaneous Compounds.

Chlorides of Uranium. Although the tetrachloride and trichloride can be obtained in a wet manner, as already described, the three chlorides of uranium are all most easily prepared in the dry way. When chlorine gas is passed over uranium the tetrachloride mixed with a little pentachloride is formed. The same two chlorides can be obtained by passing chlorine gas over a heated mixture of the oxide and carbon; a quicker method is to pass a mixture of chlorine and carbon tetrachloride over the heated oxide, for in this way oxygen is eliminated more rapidly than by solid carbon. From the mixture of tetrachloride and pentachloride the latter can be removed, owing to its greater volatility, by passing a current of carbon dioxide over the heated material. The **tetrachloride,** UCl_4, is therefore left behind in dark-green lustrous crystals. The **pentachloride,** UCl_5, is produced when chlorine is passed over the heated tetrachloride, and sublimes forward with the gas. It is a dark-red or brown substance, readily volatilizing without decomposition when warmed in a stream of chlorine; when vaporized in a stream of a neutral gas, e.g. carbon dioxide, it partially dissociates into chlorine and the tetrachloride. Both pentachloride and tetrachloride are very deliquescent. When the tetrachloride is strongly heated in a current of hydrogen, the red-brown **trichloride, UCl_3,** is produced.

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[1] G. F. Hüttig and E. von Schroeder, *Zeitsch. Anorg. Chem.* **121** (1922), 243.

Action of Light on Uranium Compounds. It has long been known that uranyl salts are decomposed by light in the presence of organic substances, being reduced to the derivatives of the lower oxides; this decomposition by light is known as *photolysis*. It is also a matter of common knowledge that solutions of uranyl salts display a brilliant greenish-yellow *fluorescence*, but that this fluorescence is destroyed by the presence of certain substances, for instance by ferric or uranous salts. Recent research appears to show that the photolysis and the fluorescence are closely connected.[1] The substances which destroy fluorescence are in general those which are capable of reacting with uranyl salts in the presence of light.

The view has been put forward that the light absorbed by uranium compounds brings about a change in the state of oxidation. According to one suggestion, the hexavalent uranium compound gives rise to a mixture of octavalent and trivalent uranium compounds:—

$$5U^{VI} + \text{light} \longrightarrow 3U^{VIII} + 2U^{III}.$$

If no substance is present which can react with either of the products, they again interact with each other, the original compound of hexavalent uranium being regenerated, and light being given out again.

$$3U^{VIII} + 2U^{III} \longrightarrow 5U^{VI} + \text{light}.$$

This causes the phenomenon which we call fluorescence; the light given out is not necessarily sent off in the same direction as that in which the original incident light was travelling, and is best observed if the eye is in such a position that the direct rays from the source of illumination do not reach it.

If, however, an organic reducing agent, like oxalic acid, is present, it will interact with the octavalent uranium salt as soon as it is formed by the light, and reduce it to the hexavalent condition without the production of light; thus the fluorescence is extinguished. Trivalent uranium compounds remain in the product and may react with the hexavalent compounds to produce compounds of an intermediate state of oxidation. The final product of the action of light on uranium oxalate is a violet-brown hydrated form of the oxide U_3O_8.

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[1] E. Baur, *Helv. Chim. Acta*, 1 (1918), 186; *Zeitsch. Elektrochem.* 25 (1919), 102; E. Baur and A. Rebmann, *Helv. Chim. Acta*, 5 (1922), 221; E. C. Hatt, *Zeitsch. Phys. Chem.* 92 (1918), 513. Compare G. Trümpler, *Zeitsch. Phys. Chem.* 90 (1915), 385.

The substances which destroy fluorescence are mostly either oxidizing agents (like ferric salts), which might be expected to react with and destroy the trivalent uranium compounds, or reducing agents (like oxalic acid, potassium iodide or uranous salts), which will react with and destroy the octavalent uranium compounds. In either case, the reverse change which is the cause of the light-evolution is prevented.

Perhaps, however, the connection between photolysis and fluorescence is best explained if we assume that the action of absorbed light is to convert the uranyl ion (or the uranium salt molecule) from an "inactive" to an "active" state, thus

$$\underset{\text{Inactive.}}{U^{VI}} + \text{light} = \underset{\text{Active.}}{U^{VI}}$$

If no reducing agent is present, the reverse change occurs the next instant, fluorescent light being emitted

$$\underset{\text{Active.}}{U^{VI}} = \underset{\text{Inactive.}}{U^{VI}} + \text{light}.$$

If, however, a reducing agent is present, it can react with the actified uranium, and reduction to a lower state of oxidation occurs; at the same time the fluorescence vanishes. Baur has worked out an interesting theory, which can be regarded as a development of that just suggested, to account for the effect of uranium salts, and of various fluorescent organic dye-stuffs, in promoting the photolytic decomposition of such substances as oxalic acid; for details, the original papers must be consulted.

Another interesting effect, which is closely connected both with photolysis and fluorescence, is the shifting of the value of the potential of the electrode

Platinum | Solution containing uranyl and uranous salts

through illumination. If a cell is set up, consisting of two platinum electrodes immersed in a solution of the uranium salts, but arranged so that one electrode (only) is exposed to a bright light, the cell can be made to furnish a current. Probably this is due to changes in the state of oxidation of the uranium brought about by the light; it is interesting to note that certain substances (mostly oxidizing and reducing agents) inhibit or hinder the production of current, and that these are in general the same substances as those which inhibit fluorescence.

Like many other fluorescent and phosphorescent substances (e.g. zinc sulphide containing a trace of manganese) solid uranium salts have the property of *triboluminescence*; that is, they emit light when crushed.

Analytical

The brown coloration obtained when potassium ferrocyanide is added to an acidified solution of a uranyl salt is characteristic of the metal. Other tests are based upon the yellow coloration obtained by the addition of hydrogen peroxide, and the green colour obtained by reduction with zinc, but several other metals show rather similar colour-changes.

Uranium is precipitated as ammonium uranate when ammonia is added to a solution of a uranyl salt. Various other metals, such as iron, are also precipitated by ammonia, but it is possible to separate uranium from all the others by digesting the precipitate with a concentrated solution of ammonium carbonate. Uranium is dissolved out as a complex carbonate, but all the other metals (including uranium X_1, which is always present in small quantities in uranium preparations which have been kept for any length of time) remain undissolved.

The filtrate can then be reacidified, boiled free from carbon dioxide, and the uranium again precipitated by means of ammonia. The precipitate of ammonium uranate yields U_3O_8 on ignition, in which form uranium can be weighed.

Terrestrial Occurrence

Many of the natural sources of uranium have been mentioned in the section on radium. Uranium occurs in the last-solidifying portions of igneous intrusions as the black oxide,

Pitchblende . . U_3O_8,

which is found in Austria (Joachimsthal), in Cornwall and elsewhere. Even more important is the secondary mineral,

Carnotite . . . . $K_2O.2UO_3.V_2O_5.3H_2O$,

found in Colorado and Utah as a yellow impregnation in sandstone. Rather similar uranium minerals occur in a complex ore found at Olary in Australia.

Other minerals containing small quantities of uranium include the impure oxide of thorium,

Thorianite ThO_2
and Euxenite a niobate-titanate of cerium, yttrium, erbium and uranium,

both of which have already been mentioned.

All minerals containing uranium contain also small quantities of radium, formed in the past ages by the decay of uranium atoms. Where the conditions have been such that the radium produced has not been removed mechanically, the radium content is always 1/3,000,000 of that of the uranium.

TECHNOLOGY AND USES

The whole of the uranium compounds produced are bye-products of the radium industry. The methods of working up the American carnotite and the Australian complex ores have already been discussed in the section on radium. The uranium is separated from the solution of the ore in acid by precipitation with sodium carbonate, insoluble sodium uranate being thrown down. From this precipitate, other uranium compounds can readily be produced. For instance, the black oxide (UO_2) is made by fusion of sodium uranate with salt [1] and charcoal in an iron pot. By dissolving the sodium uranate in acids, uranyl salts may be obtained. Uranyl nitrate is one of the best-known salts of uranium. It yields uranic oxide (UO_3) when gently ignited.

The chief use of uranium is at present in the manufacture of yellow glass and glaze. For this purpose, sodium uranate is often employed. But the demands of the glass and ceramic industries do not provide sufficient use for the comparatively large amounts of uranium obtained in the radium industry. Great hopes have been based upon the extensive use of uranium in the steel industry. Much has been written concerning uranium steel,[2] but the reports are somewhat contradictory. Uranium steel was actually employed during the war (mainly in Germany) for the manufacture of large guns. It still seems doubtful whether uranium steel possesses any properties which cannot equally well be obtained by the use of special steels containing other metals, but it would appear at least to be capable of being used as a good substitute for other alloy steels. The uranium is added to the steel as the alloy *ferro-uranium*, made by heating the black oxide of uranium and oxide of iron with carbon in the electric furnace. Some difficulty was met with at first in producing a ferro-uranium with a sufficiently low carbon-content, but the manufacture of an alloy of iron and uranium in nearly equal proportions and with a carbon content of less than 5 per cent. has now been achieved in America.[3]

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[1] C. L. Parsons, *J. Ind. Eng. Chem.* 9 (1917), 466.

[2] E. Polushkin, *Rev. Met.* 17 (1920), 421; H. W. Gillet and E. L. Mack, *J. Ind. Eng. Chem.* 9 (1917), 342; E. Polushkin, *Carn. Schol. Mem.* **10** (1920), 129.

[3] R. M. Keeney, *Bull. Amer. Inst. Min. Eng.* **140** (1918), 1321.

Uranium carbide has been tested as a catalyst for the production of ammonia by direct combination of nitrogen and hydrogen under pressure, and so long as the two gases are quite pure it is very efficient; the carbide gradually becomes converted to nitride, but this change actually renders it more efficient, since it is accompanied by "crumbling" and consequent increase of the active surface. However, the catalyst is very liable to "poisoning" if the gases used are impure, and is not used in practice at the present time.

Uranium has been used to a very small extent in photography. An ordinary bromide print, with a cold black image consisting of metallic silver, can be given a warm reddish colour by immersion in a solution of uranyl ferricyanide, or—what is equivalent to it—a solution containing both uranyl nitrate and potassium ferricyanide. The silver reduces the uranyl ferricyanide, and red-brown uranyl ferrocyanide—which is insoluble—is deposited where the silver was before. The same solution is also used as an "intensifier" for the treatment of thin negatives, the uranium ferrocyanide image being more opaque to actinic rays than the corresponding silver image.

Sensitive printing papers containing uranium salts—which are decomposed when exposed to light—are easy to prepare, but are not used to any appreciable extent.

GROUP VIIA

	Atomic Weight.
Manganese	54·93
Element between molybdenum and ruthenium (perhaps Ogawa's *nipponium*), about	100
Missing Element between tungsten and osmium, about	188

Of the possible elements of Group VIIA, only one, manganese, is known with certainty. The gaps in the Periodic Table evidently represent two rather rare elements, and there is little doubt that these gaps will be filled. It is indeed quite possible that the lower element, which should fall between molybdenum and ruthenium, may be represented by a new element which Ogawa [1] claims to have found in thorianite and molybdenite, and to which he has given the name *Nipponium*. This metal is said to resemble molybdenum fairly closely, and exists in two states of oxidation. The higher oxide is analogous to MoO_3, and has acidic properties, whilst the lower one has a basic character. The solution of the chloride seems to be yellow-green in colour. The salts are precipitated by ammonia in presence of ammonium chloride, the precipitate obtained being soluble in caustic alkali. The equivalent weight appears to be about 50, which would suggest an atomic weight of 100, and this would cause the element to fall into the place between molybdenum and ruthenium.

This description of nipponium, if confirmed, would appear to fill the lower gap. Another observer [2] had independently found evidence of a new element in thorianite, but had ascribed it to the tin group. The properties assigned to it, however, are generally similar to those ascribed by Ogawa to nipponium, and it is probably the same element.

There remains the question of the element between tungsten and osmium. This appears to be undiscovered, although a new element —to which the name *Canadium* was applied—was reported some years ago to have been found in a platinum ore in British Columbia.[1] The properties described differ from those of nipponium, and resemble rather those of the metals of the platinum group. However, the very existence of canadium is extremely doubtful, other investigators having failed to find it in the same ore.

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[1] M. Ogawa, *J. Coll. Sci. Tokyo*, 25 (1908), Arts. 15, 16.

[2] C. de B. Evans, *Trans. Chem. Soc.* 93 (1908), 666.

We are left, therefore, with manganese as being the only "certain" member of the group. It will be convenient at this point to call attention to the general similarity between manganese and the metals of Group VIA. As in that group, coloured compounds are common. The full valency of manganese (seven) is only reached in one class of compounds, which, although surprisingly stable in the solid state, are powerful oxidizing agents in solution; classes of compounds corresponding to lower valencies, namely six, four, three and two, are known, the latter being the most stable.

On the other hand, manganese has much in common with iron, which stands on the other side of it in the table. Not only are many of the manganese compounds very similar to the corresponding compounds of iron, but also magnetism—one of the most remarkable features of iron—is met with in several materials containing manganese. The boride (MnB), phosphide (MnP) and two antimonides (MnSb and Mn_2Sb) are distinctly magnetic, whilst certain alloys containing manganese, copper and aluminium (or tin) have remarkable magnetic properties.

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[1] A. G. French, *Chem. News*, **104** (1911), 283.

MANGANESE

Atomic weight 54·93

The Metal

Pure manganese is a grey-white metal, capable of taking a good polish; it possesses a faint but distinct reddish tinge; the presence of carbon renders it rather darker. When pure it is not hard enough to scratch glass, but the presence of carbon and silicon increases the hardness considerably, and most samples of manganese actually scratch steel. The melting-point of the pure metal is probably about 1,260°C. It is quite volatile at temperatures a little above the melting point. In this respect manganese presents a contrast to the highly refractory metals of the last group. The specific gravity is 7·4.

The finely divided metal oxidizes quickly when exposed to the air, and must be preserved under oil. The compact metal does not suffer any noticeable change, even when exposed to a damp atmosphere, becoming no doubt protected by an invisible oxide-film. Heating in air, however, causes rapid oxidation.

No doubt on account of the obstructive nature of the oxide-film, manganese reacts slowly with cold water, and much more rapidly with boiling water. If immersed in a dilute acid—even acetic acid—it evolves hydrogen very readily.

Laboratory Preparation. It is possible to deposit manganese electrolytically from a cool aqueous solution of manganous sulphate containing a trace of free acid.[1] If too much acid is present, the current efficiency is very low, practically all the current being employed in the production of hydrogen. If too little acid is present, the deposit is spongy, and contains much hydroxide. The current density must be rather high, so as to depress the cathode potential to the value (about − 1·1 volts) required for the deposition of the metal. It is noteworthy that a considerable deposit of furry brown manganese dioxide is often formed during electrolysis on the anode.

Although the electrolytic method of producing manganese is of considerable interest, the product is dark grey, powdery, and tends to contain oxide. If a mercury cathode is employed, a manganese amalgam is obtained; on distilling off the mercury *in vacuo* at about 250° C., the manganese is said to be left behind as a finely divided pyrophoric powder.[1]

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[1] G. D. van Arsdale and C. G. Maier, *Trans. Amer. Electrochem. Soc.* **33** (1918), 109.

However, where manganese is required in any quantity, dry methods of preparation are preferable. The metal can, for instance, be prepared by reduction of the oxide with aluminium according to the "thermite reaction"; but the product obtained by this method usually contains about [illegible] per cent. of aluminium, although the quantity can be reduced if the mixture employed for the reaction contains excess of manganese oxide. Reduction with carbon yields a metal containing an appreciable quantity of the latter element. A purer product is said to be obtained by reducing the dioxide in hydrogen under high pressure (150 atmospheres) at 2,500° C., but naturally special apparatus is required for this method.[2]

Compounds

The compounds of manganese correspond to the five oxides, MnO, Mn_2O_3, MnO_2, MnO_3, and Mn_2O_7. The first two oxides are basic, the last two acidic in character, whilst the middle oxide (MnO_2) has both feeble acidic and feeble basic properties. There is another intermediate oxide, Mn_3O_4.

A. Compounds of Divalent Manganese (Manganous Compounds).

The **oxide,** MnO, is formed when any of the higher oxides are ignited in hydrogen. It is pale green in the anhydrous condition. The corresponding **hydroxide,** $Mn(OH)_2$, is formed when a manganous salt solution is made alkaline with caustic soda; it comes down as a white precipitate, but quickly becomes brown when exposed to the air, owing to the formation of the higher hydroxides.

The **manganous salts** are formed by the action of the appropriate acids upon manganese or manganous hydroxide. The solutions, and in many cases the solid salts, have a pink colour. It is, however, noteworthy that the intensity of the pink colour of a given salt often varies considerably in different samples, some having a very noticeable rose hue, whilst other samples of the same salt may appear colourless. The more intensely coloured preparations probably owe their abnormal colour to a trace of manganic salt. It has been suggested that pure manganous salts are really colourless; but it is more likely that even pure manganous salts possess a faint pink tint, and that the apparently "colourless" samples, which have been described from time to time, contained a trace of nickel salt, the green colour of the nickel masking the pink colour of the manganous salt.

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[1] Guntz, *Bull. Soc. Chim.* 7 (1892), 275.

[2] E. Newbery and J. N. Pring, *Proc. Roy. Soc.* 92 [A] (1916), 277.

The **sulphate,** $MnSO_4.7H_2O$, separates in pink crystals from the solution of the metal or the hydroxide in sulphuric acid when cooled below 6° C. Other hydrates with 2, 3, 4 and 5 molecules of water are known; the pentahydrate, for instance, is usually obtained when the crystallization is conducted between 7° and 20° C. The **nitrate,** $Mn(NO_3)_2.6H_2O$, is hygroscopic. The **chloride,** $MnCl_2.4H_2O$, is obtained from a solution of the hydroxide in hydrochloric acid. When heated in air it evolves chlorine, to some extent, an oxide being produced. The anhydrous salt, however, can be obtained by heating the hydrated chloride in a current of hydrogen chloride.

Manganous salts have reducing properties, especially in the presence of alkali. Manganous sulphate, for instance, added to ammoniacal silver nitrate causes a precipitate of metallic silver.[1]

The insoluble manganous salts are obtained by precipitation. Of these the **carbonate** is a white precipitate, turning brown, through oxidation, when exposed to the air. The **phosphate** is a pink precipitate.

Manganous sulphide, MnS, is obtained when an ammoniacal solution of a manganous salt is treated with ammonium sulphide in the presence of ammonium chloride. It usually comes down as a pink precipitate, but under certain conditions this slowly changes to a green form of the sulphide. The velocity of the change depends on the concentration of manganous salt and ammonia present.[2] The conversion seems to proceed best in the presence of rather concentrated and distinctly ammoniacal solutions. The pink form is also converted to the green form when heated in a current of carbon dioxide or hydrogen sulphide at about 320° C.

B. Compounds of Trivalent Manganese (Manganic Compounds)

Manganic oxide, Mn_2O_3, is formed when manganese dioxide or manganous nitrate, carbonate, or oxalate is ignited in air below 940° C.; it is then obtained as a brown powder. If the temperature rises above 940° C., further oxygen is evolved, and the oxide, Mn_3O_4, is left. The **hydroxide** is produced by the hydrolysis of the corresponding sulphate, and is a brown precipitate; it can also be prepared through the oxidization of a solution of manganous chloride containing ammonia and ammonium chloride by bubbling air through the liquid.[1] The formula MnO(OH) has been assigned to the hydroxide, but in the precipitated form the water-content is naturally somewhat variable.

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[1] V. Macri, *Boll. Chim. Farm.* **58** (1919), 201; Abstract, *J. Chem. Soc.* **116** (1919), ii. 467.

[2] V. M. Fischer, *J. Russ. Phys. Chem. Soc.* **46** (1914), 1481 (Abstract, *J. Chem. Soc.* **108** (1915), ii. 482), describes in detail the conditions which should be observed to obtain the green form.

Manganic oxide has weak basic properties, but the salts are unstable, tending on the one hand to hydrolyze, and, on the other hand, to become reduced to manganous derivatives. The oxide—as commonly produced—dissolves only slowly in sulphuric acid. The **sulphate,** $Mn_2(SO_4)_3$, is more conveniently produced by heating the dioxide (MnO_2) with sulphuric acid, oxygen being evolved. The product is separated from excess of sulphuric acid on a porous tile, and may be washed with nitric acid. The sulphate is a green solid, yielding a violet solution, which, however, readily suffers hydrolysis, yielding the brown precipitate, MnO(OH), mentioned above. Certain double salts, notably the cæsium and rubidium alums (e.g. $Cs_2SO_4.Mn_2(SO_4)_3.24H_2O$), which have fairly low solubilities, can be prepared in a pure state; they form pink-red octahedra.

The question of the existence of the corresponding chloride, $MnCl_3$, is discussed later.

C. Compounds of Tetravalent Manganese.

When manganous carbonate is heated in air at a comparatively low temperature (250° C.), it loses carbon dioxide and takes up oxygen, the black **dioxide,** MnO_2, being formed. The same oxide is produced in a brown hydrated form when manganous hydroxide is treated with an oxidizing agent, such as chlorine or sodium hypochlorite. Again a hydrated form of the dioxide is precipitated on the anode when a hot solution of manganous sulphate is electrolysed.

The dioxide enters readily into the state of colloidal solution. Colloidal solutions are under certain conditions produced when the dioxide is obtained through the oxidation of a manganous salt solution, but are more conveniently prepared by the reduction of a permanganate. Thus fairly dilute $\left(\frac{M}{100}\right)$ potassium permanganate when treated at 90–100° C. with concentrated ammonia yields a coffee-brown "sol" of manganese dioxide, although if a concentrated solution of the permanganate is employed the dioxide is thrown down as a brown precipitate.[2]

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[1] J. Meyer and R. Nerlich, *Zeitsch. Anorg. Chem.*, 116 (1921), 117.

[2] E. J. Cuy, *J. Phys. Chem.* 25 (1921), 415.

When solutions containing compounds of divalent and heptavalent manganese, for instance manganese sulphate and potassium permanganate, are mixed together in the presence of an electrolyte, such as potassium nitrate, zinc sulphate or copper sulphate, a brown precipitate is obtained; this precipitate contains tetravalent manganese, and may be regarded as hydrated manganese dioxide, although it usually contains potassium, zinc or copper. The reaction can be expressed,

$$3MnO + Mn_2O_7 = 5MnO_2.$$

The precipitate obtained in the presence of copper sulphate has been described as "copper manganite." It seems probable that it is merely an adsorption product. The function of the electrolyte appears to be to bring about the flocculation of the colloidal solution of manganese dioxide, which is the first product.[1]

The basic properties of manganese dioxide are somewhat feebly developed. When heated, for instance, with sulphuric acid, manganese dioxide evolves oxygen and passes into solution, manganic sulphate ($Mn_2(SO_4)_3$) being formed. Brown solutions of the **disulphate**, $Mn(SO_4)_2$, can, however, be obtained by the anodic oxidation of manganous sulphate in the presence of sulphuric acid; the disulphate is very soluble, and difficult to isolate in the solid state.[2]

In cold hydrochloric acid the dioxide dissolves with the evolution of some chlorine. A brown solution is obtained, which probably contains a certain amount of undecomposed tetrachloride, $MnCl_4$, but would seem to contain chiefly the trichloride (manganic chloride), $MnCl_3$. When the solution is heated, more chlorine is evolved, and on evaporation manganous chloride ($MnCl_2$) is the only solid chloride obtained. If, however, instead of being evaporated, the solution is cooled in a freezing-mixture, saturated with hydrogen chloride and treated with potassium chloride, a dark-red double salt, $MnCl_3.2KCl.H_2O$, is obtained in the solid state. Derivatives of the tetrachloride must be obtained in another way. When powdered potassium permanganate ($KMnO_4$ or $K_2O.Mn_2O_7$) is dissolved in "glacial" acetic acid, reduction occurs, a brown solution containing derivatives of trivalent and tetravalent manganese being obtained. When hydrogen chloride is passed into this solution, the unstable double chloride $MnCl_4.2KCl$, is produced as an almost black crystalline precipitate.[3]

One of the most easily produced salts of tetravalent manganese is the **double iodate**, $Mn(IO_3)_4.2KIO_3$ or $K_2[Mn(IO_3)_6]$, which is produced as a coarse brown-violet powder when manganese dioxide is treated with a hot solution of iodic acid containing potassium iodate. Its comparative stability is no doubt connected with the fact that it is comparatively insoluble.

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[1] P. B. Sarkar and N. R. Dhar, *Zeitsch. Anorg. Chem.* **121** (1921), 135.

[2] M. Sem, *Zeitsch. Elektrochem.* **21** (1915), 426.

[3] R. J. Meyer and H. Best, *Zeitsch. Anorg. Chem.* **22** (1899), 169.

The acidic character of manganese dioxide is more pronounced than the basic character, but the **manganites**, as the salts formed with bases are termed, are mostly insoluble. The brown precipitates formed when hot solutions of potassium permanganate and manganous sulphate are mixed in the presence of a salt of a heavy metal have been described as "manganites," but it is doubtful whether they represent definite compounds; they are probably adsorption products. More characteristic manganites are obtained from the manganates (the derivatives of the higher oxide, MnO_3), which are comparatively unstable except in alkaline solution. When a stream of carbon dioxide is passed through a solution of potassium manganate, the manganate decomposes and a **potassium manganite**, $K_2Mn_5O_{11}$, or $K_2O.5MnO_2$, appears as a yellow precipitate. Manganites are also formed by oxidation from the lower oxide. When hydrated manganous oxide is oxidized by air in the presence of calcium hydroxide, or is treated with bleaching powder containing excess of lime, calcium manganite is produced.

D. Compounds of Hexavalent Manganese.

Derivatives of manganese trioxide (MnO_3), known as the **manganates**, are formed when manganese dioxide is fused with a caustic alkali under oxidizing conditions, or in the presence of an oxidizing agent. For instance, if manganese dioxide is mixed with potassium hydroxide and potassium nitrate, and the mixture is heated to fusion, a green mass is obtained. This yields a green solution, from which the green salt, **potassium manganate**, $KMnO_4$, can be isolated by crystallization. The manganates of the alkali metals are, however, rather difficult to prepare pure, being extremely soluble. They are powerful oxidizing agents.

The manganates (e.g. K_2MnO_4) correspond in formula to the sulphates (e.g. K_2SO_4), and it is not surprising to find that potassium manganate is isomorphous with potassium sulphate, and, according to some authorities, sodium manganate with sodium sulphate.[1] The solubility relations of the salts are also rather similar, the manganates of the alkaline-earth metals being nearly insoluble.

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[1] J. G. Gentele, *J. Prakt. Chem.* 82 (1861), 58, claimed to have isolated sodium manganate, $Na_2MnO_4.10H_2O$, in crystals isomorphous with Glauber's salt, $Na_2SO_4.10H_2O$. But R. Funk, *Ber.* 33 (1900), 3696, suggests that the crystals obtained by Gentele actually *consisted of* Glauber's salt, with some included manganate solution. Funk failed to isolate the manganate from the solution.

Solutions of the manganates are fairly stable in the presence of free alkali, but become unstable if acidified, a permanganate being produced, together with manganese dioxide or a manganite. Even carbon dioxide—as has been stated above—can bring about this change, the green colour of the solution changing to deep red (due to the permanganate), whilst a brown or yellow precipitate (the dioxide) appears.

Since, therefore, the manganates are decomposed so readily by acids, the preparation of the free oxide (MnO_3) is clearly one of some difficulty. It is commonly described as being present in the pink fume evolved, along with much carbon dioxide, when a solution of potassium permanganate in concentrated sulphuric acid is dropped on to dry sodium carbonate. But an investigation into the subject has indicated that the so-called "trioxide" obtained by this method is really an impure hydrated permanganic acid.[1] The trioxide must therefore be regarded as being unknown.

E. Compounds of Heptavalent Manganese.

It has been stated that the manganates are stable in the presence of alkalis, but that when treated with acids they tend to pass into the **permanganates**, derivatives of the heptoxide, Mn_2O_7, the dioxide (or a derivative) being formed at the same time. This change can be expressed thus :—

$$3MnO_3 = Mn_2O_7 + MnO_2.$$

When, however, an oxidizing agent as well as an acid is added to the manganate solution, the manganese is converted completely to the heptavalent condition without any precipitation of dioxide or manganite. Permanganates are also formed by the oxidation of a manganous salt by lead peroxide in presence of free nitric acid and a salt of an alkali-metal. The permanganates can be produced from metallic manganese by electrolysis of caustic alkalis using the manganese as anode ; if the cathode is of platinum, and a little calcium hydroxide is added to the solution, a film is formed over the cathode, and this film prevents the cathodic destruction of the permanganate produced at the anode.[2]

The deep purple-red solution of a permanganate deposits the solid salt when concentrated and cooled. **Potassium permanganate**, $KMnO_4$, forms long rhombic prisms, very dark and possessing an almost metallic lustre ; its solubility is only about

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[1] F. R. Lankshear, *Zeitsch. Anorg. Chem.* 82 (1913), 97.

[2] C. O. Henke and O. W. Brown, *J. Phys. Chem.* 24 (1920), 608.

4 per cent. at 15° C., and it can easily be obtained in a pure state by crystallization.

All solutions of permanganates are powerful oxidizing agents. They convert ferrous salts to ferric and readily destroy many organic substances, oxidizing them to carbon dioxide. When the oxidation occurs in the presence of acids, permanganates become reduced to manganous salts; in neutral or alkaline solutions, on the other hand, manganese dioxide is produced, which itself possesses a slow oxidizing power. Several of the reactions are catalytically aided by the presence of lower manganese compounds. For instance, in a warm acidified solution, permanganate oxidizes oxalic acid to carbon dioxide. At ordinary temperatures the reaction does not start of its own accord, but can be brought about, without warming, if a manganous salt is added to the solution. Of course, when once started, the reaction proceeds more quickly, since manganous salts are actually formed in the change. In other cases, manganese dioxide has been noticed to cause a catalytic acceleration to the oxidizing action of permanganate.

The **oxide,** Mn_2O_7, from which the permanganates are derived, can be prepared by adding pure potassium permanganate to sulphuric acid (diluted until it has the composition, $H_2SO_4 + H_2O$), and heating the green liquid to 60–70° C. A violet vapour arises and may be condensed in a well-cooled receiver, a heavy dark-green liquid being obtained. The oxide decomposes when heated above 70° C., often with explosive violence. It dissolves in water, forming a purple liquid which no doubt contains permanganic acid. The heptoxide is a very powerful oxidizer; and a violent explosion occurs if it comes into contact with organic matter such as alcohol, ether or even paper. The corresponding **permanganic acid,** $HMnO_4$, is more stable. The solution is easily produced by adding sulphuric acid to a solution of barium permanganate, and filtering off the barium sulphate. When the solution, which has the colour of the permanganates, is allowed to evaporate in air, violet-blue crystals of permanganic acid, always mixed with brown lower oxides, are obtained.[1]

Manganese heptoxide is fairly soluble in concentrated sulphuric acid, a green liquid being obtained which turns to the familiar violet-red colour of permanganic acid when diluted. It is suggested that the green liquid may contain a basic sulphate, on the assumption that the oxide, Mn_2O_7, has feeble basic properties. The basic sulphate has not been isolated, but a **basic chloride,** MnO_3Cl, is obtained by adding absolutely dry sodium chloride to the green solution of potassium permanganate in concentrated sulphuric acid. The basic chloride distils away as a greenish vapour, which, if led through a tube surrounded by a freezing mixture, condenses to a green-brown liquid, with an unpleasant chlorine-like odour. It is at once hydrolysed by water, hydrochloric and permanganic acids being produced.

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[1] M. M. P. Muir, *Trans. Chem. Soc.* 91 (1907), 1485.

F. Intermediate Oxide of Manganese.

The oxide, Mn_3O_4, intermediate between MnO and Mn_2O_3, is formed when either of the other oxides is heated in air above 940° C., or in oxygen above 1,090° C. (the pressure is assumed to be 760 mm.). It is a reddish-brown substance. No derivatives are known. When treated with cold concentrated sulphuric acid it yields a mixture of manganous and manganic sulphates, and may thus be looked upon as a manganous-manganic oxide, $MnO.Mn_2O_3$. On the other hand, hot dilute sulphuric acid only partially dissolves it, manganous sulphate being produced, while the dioxide (MnO_2) is left behind; this would suggest the formula $2MnO.MnO_2$. The red oxide of manganese is by no means the only inorganic compound which behaves as though it possessed two distinct constitutions.

Analytical

The wide range of colour found among the manganese compounds suggests numerous tests for the metal. Manganous compounds are oxidized to the green manganate when fused with potassium nitrate; the green solution obtained on dissolving the mass in water becomes deep purple-red on being acidified, a permanganate being formed. Quite small traces of manganese in other bodies can be detected by boiling with nitric acid and lead peroxide, the pink colour of a permanganate being observed in this case after the excess of lead peroxide has settled to the bottom. The permanganates evolve oxygen when treated with hydrogen peroxide in acid solution, becoming reduced to manganous salts.

The manganous salts give a white precipitate with sodium hydroxide, which darkens when exposed to the air; they yield a flesh-coloured precipitate with ammonium sulphide in the presence of ammonia. A trace of manganese salt fused in a borax bead in the oxidizing flame imparts an amethyst colour to the bead, the colour being probably due to manganic borate. In the reducing flame the colour disappears, manganous borate being no doubt formed.

Manganese is not precipitated from an acidified solution by sulphuretted hydrogen, and thus all the metals (like lead and mercury) which are precipitated under these circumstances can be separated from it. Under ordinary circumstances, manganese is not precipitated by ammonia in the presence of ammonium chloride; but if other metals are present whose hydroxides are thrown down under these conditions, for instance, ferric iron, chromium or aluminium, the precipitate will carry down with it a certain amount of manganese. Moreover if air has access to the solution, higher oxides of manganese—which are less soluble—will be precipitated to some extent. Consequently, the separation of iron and the other metals from manganese by ammonia is never complete, and the precipitate must be redissolved in acid and the metals precipitated with ammonia a second time. The two filtrates are mixed together, and should—if proper precautions have been taken—contain nearly all the manganese, free from iron, chromium and aluminium.

Much work has been devoted to finding a more satisfactory method of separation based upon the use of some precipitant, which, being less strongly alkaline than ammonia, will be less likely to allow of the precipitation of manganese hydroxide. If iron and aluminium only are to be separated from manganese, they may be precipitated as basic acetates. Sufficient sodium carbonate must first be added to give a slight opalescence (so as to ensure the neutralization of any free acid present), and the slight precipitate is afterwards dissolved with a drop of hydrochloric acid. Excess of sodium acetate is then added, and the solution is boiled. All the iron and aluminium are precipitated, whilst practically all the manganese remains in the solution, although, even here, most analysts, for accurate work, prefer to repeat the precipitation.[1]

If the solution contains no sulphate, the iron, chromium and aluminium may be removed by a suspension of barium carbonate to a neutral or faintly acid solution; iron, chromium and aluminium come down as hydroxides, but the manganese remains in solution. The operation must be conducted at ordinary temperatures, and requires some hours, frequent shaking being advisable. The method is said to be more reliable than the acetate method when aluminium is to be separated from manganese.

Having removed iron, aluminium and chromium, we next proceed to remove zinc, nickel and cobalt. The usual method of separation of these metals depends on the different conditions of formation of the respective sulphides.[2] In the presence of ammonia all four sulphides are precipitated by hydrogen sulphide. Zinc sulphide—the most insoluble of the four—can be precipitated from a cold solution containing free acetic acid (or even a trace of free sulphuric acid); if the filtrate is then treated with excess of ammonium acetate—which serves to reduce the hydrion concentration—nickel and cobalt sulphides may also be precipitated by hydrogen sulphide (at 70–80° C.). Manganese, however, still remains in solution in either case, owing to the comparatively great solubility of manganese sulphide. It can afterwards be precipitated as sulphide from a solution containing excess of ammonia.

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[1] See, however, A. Mittasch, *Zeitsch. Anal. Chem.* 42 (1903), 492, for particulars of a single-precipitation method.

[2] For details see F. P. Treadwell, "Analytical Chemistry"; translation by W. T. Hall (Chapman & Hall); also W. W. Scott, "Standard Methods of Chemical Analysis" (Crosby, Lockwood). The different separation processes are conveniently brought together by A. Rüdisüle, "Nachweiss, Bestimmung und Trennung der chemischen Elemente" (Haupt).

The sulphide can be ignited in air and thus converted to the oxide Mn_3O_4, which can then be weighed. If, however, a large quantity of sulphide is present, the conversion to oxide by heating presents difficulty, and it is better to redissolve the precipitate in acid, and to reprecipitate the metal as carbonate, which readily yields the oxide Mn_3O_4 on ignition. The final ignition must be conducted in a porcelain crucible entirely surrounded by the flame of a Teclu burner. Otherwise the residue may contain more oxygen than corresponds to the formula Mn_3O_4.

On account of the possibility of variation in the composition of the oxide, some authorities prefer to treat the residue with sulphuric acid, excess of which is cautiously driven off by placing the crucible inside a larger crucible, which is then heated to redness; the product is cooled in a desiccator and weighed as the anhydrous sulphate, $MnSO_4$.[1]

The methods of separation given above are somewhat troublesome, and quicker methods are needed for technical analysis. If manganese is present in neutral solution as a manganous salt, free from other oxidizable substance, the amount can be determined roughly by titration with potassium permanganate in presence of zinc sulphate. Under these circumstances, manganese dioxide (MnO_2), or a manganite, is precipitated, and by observing how much permanganate must be added before the appearance of a pink colour shows it to be present in excess, the amount of manganous salt present can be calculated.

For estimating the amount of manganese in steel, a rapid method is often used, which may shortly be described. The steel is dissolved in sulphuric acid and boiled with nitric acid and lead peroxide (free from manganese), which oxidizes the manganese to permanganic acid. The excess of lead peroxide is filtered off, and the permanganate determined by titration with hydrogen peroxide which has previously been standardized against permanganate of known strength. A variation of the process depends on the use of potassium bismuthate instead of lead peroxide; the bismuthate gives more certain results, and can be obtained more easily free from manganese.

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[1] F. A. Gooch and M. Austin, *Zeitsch. Anorg. Chem.* 17 (1898), 264.

Manganese, like lead and thallium, but unlike most other metals, can be deposited by electrolysis on the *anode*, as an oxide. Advantage may be taken of this fact in the estimation of manganese.[1] If a hot solution of the manganous salt, containing sodium acetate and chrome alum, is electrolysed for 25 minutes, a roughened platinum dish being used as anode, and a rotating perforated disc being employed as cathode (the reversal of the usual arrangement), the manganese is completely thrown down as a hydrated dioxide. A fairly high current density is needed so as to make the anode potential sufficiently positive. After the electrolysis, the dish is dried and then strongly ignited. The manganese dioxide (MnO_2) is thus converted to Mn_3O_4, the colour changing from deep sepia to reddish-brown. When the deoxidation, which is rather slow, is complete, the dish is weighed. The process is, however, not completely satisfactory, and it is difficult to ensure that the oxide weighed has the exact composition Mn_3O_4.

The function of the chrome alum in the anodic precipitation of manganese is of interest. If it be omitted the coating of peroxide is apt to be brittle. Apparently, the chrome alum serves to restrain the evolution of oxygen in bubbles, which would cause unsuitable physical qualities in the peroxide deposit. In the place of the evolution of oxygen gas, the chromium salt becomes oxidized to chromic acid. Other oxidizable substances—such as alcohol—can be used instead of chrome alum.

Since most other metals are not easily deposited upon the anode, it might be thought that electrolysis would provide a means of readily separating manganese from other metals, e.g. iron. Such a separation is possible, but is not quite exact, since when manganese dioxide is precipitated anodically in the presence of iron, small amounts of ferric hydroxide are liable to come down with it. Ammonium acetate and formic acid are added to a solution containing iron and manganese as sulphates, and the solution is electrolysed at ordinary temperature for 5 hours without stirring. The manganese is deposited as dioxide on the anode, and is afterwards ignited and weighed as Mn_3O_4. The iron is deposited as metal on the cathode, but, since it is likely to contain carbon, it is best not to weigh it directly, but to dissolve it once more in acid, and determine it volumetrically.[2]

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[1] C Engels, *Zeitsch. Elektrochem.* **2** (1896), 413; **3** (1897), 286.

[2] G. P. Scholl, *J. Amer. Chem. Soc.* **25** (1903), 1054.

TERRESTRIAL OCCURRENCE

The manganese of the original rock magma has crystallized out in all parts of the rocks, but mainly in the comparatively basic portions. Thus many analyses of gabbros and diabases show 0·1–0·2 per cent. of manganese, whilst those of granite usually show quantities below 0·05 per cent. In either case, the manganese does not occur, for the most part, in special manganese minerals, but tends partially to replace other metals in common minerals, of which it is not an essential constituent. For instance, many samples of hornblende contain 0·5–1·0 per cent. of manganese, although others contain only a trace; the manganese atoms—where they occur—probably replace a similar number of magnesium or calcium atoms, playing the same part in the crystal structure. In garnet, again, manganese often partially replaces iron, and in some varieties displaces it altogether. In addition, manganese is often present in the thermal waters that arise from igneous masses.

When rocks containing manganese undergo weathering, the manganese readily passes into solution; the dissolution occurs most easily in the presence of acids such as carbon dioxide or sulphuric acid (the latter derived from the oxidation of pyrites), manganous bicarbonate or sulphate being then produced. If, subsequently, through contact with basic substances like limestone, or through other causes, the water carrying manganese ceases to be acid, the manganese will generally be precipitated as carbonate or hydroxide, which may afterwards become dehydrated, yielding the oxide. Thus we get the minerals,

Rhodochrosite . . .	$MnCO_3$
Pyrochroite . . .	$Mn(OH)_2$
and Manganosite . . .	MnO

All of these minerals are liable to subsequent change through oxidation. Rhodochrosite is also found in veins, along with the ores of other metals, having been deposited from ascending thermal waters.

Far the more common factor, however, in causing the precipitation of manganese from solution is the presence of oxygen. The higher oxides of manganese are less basic than manganous oxide, and the effect of dissolved oxygen in the water will be to throw down one of the higher hydroxides. Here, again, the minerals will often lose water during subsequent ages. Thus we get such minerals as

Manganite	$Mn_2O_3.H_2O$
Braunite	Mn_2O_3
Hausmannit	Mn_3O_4
Pyrolusite and Polianite	MnO_2

Of these pyrolusite is the most important ore of manganese.

Since the manganese is usually precipitated fairly rapidly from the solution, it is natural to find that the minerals are in many cases earthy, brown, amorphous substances. In other cases, however, firm masses are met with; braunite and hausmannite form comparatively hard crystalline aggregates of a dark brown colour and sub-metallic lustre. Pyrolusite is softer, and is black, with metallic lustre, crystallizing in the rhombic system; polianite, the other form of the dioxide, is tetragonal, isomorphous with rutile (TiO_2) and cassiterite (SnO_2).

Very favourable conditions for the precipitation of manganese occur in bogs and shallow lakes. Where waters rising in hills composed of igneous rocks containing manganese, pass into a swamp or lake, and remain stagnant or only slowly moving, the oxygen has plenty of time to diffuse into the shallow layers of water, and higher hydroxides will be formed, perhaps at first as a colloidal solution, but finally as a precipitate which will sink to the bottom of the lake or pools. In this way earthy " wad " or " bog-ore " is produced.

It is, however, necessary to point out that iron is leached out from rocks by weathering under exactly the same conditions as manganese, and is also liable to be deposited (as ferric hydroxide) through the action of dissolved oxygen. The manganese ores referred to above almost always contain some iron; but fortunately the precipitation of most of the iron occurs—as a general rule—prior to the precipitation of manganese, and a considerable separation of the two elements takes place. It is, however, obvious that many other substances may be deposited with the manganese. The name " psilomelane " is rather loosely applied to impure hydrated ores of manganese, often earthy. Some varieties contain much barium, others zinc, others again cobalt.

The most important deposits of manganese ore occur in the Caucasus, India, Brazil, the United States, Cuba, and Spain; the ore is also found in the Sinai Peninsula and in West Africa.

Some manganese ores are certainly residual in origin, representing the remains of the weathered igneous rock left on the spot after the water has done its work. Certain Brazilian and Indian deposits are of this character, but clearly only an igneous rock exceptionally rich in manganese will leave useful ores after weathering.

The mineral

Franklinite $(Fe,Zn,Mn)O,(Fe,Mn)_2O_3$

which occurs in New Jersey at the junction of limestone and granitic dykes, is of more importance as an ore of zinc than of manganese, and the discussion of its mode of origin may be deferred until the section dealing with zinc.

Technology and Uses

Before the war, the greater part of the world's demand for manganese was supplied from the Caucasus and India, with smaller amounts from Brazil and Germany. The cutting off of the Russian and German supplies from Western Europe and America in 1914—coinciding with an exceptional demand for the metal for armaments—was the occasion for great efforts to develop the ore-fields of Brazil, the United States, Cuba, and Spain, and the production of these countries increased in a sensational manner. At the end of the war, the demand for manganese dropped very much, and the industry in all these countries declined, in spite of the fact that production at the Caucasian mines was at a standstill—owing to the unsettled state of the district.[1]

Manganese in Steel. By far the largest demand for manganese has always been due to its use in the steel industry. For this purpose, alloys containing both manganese and iron, which are called **ferro-manganese** when rich in manganese, and **spiegeleisen** when poor, are utilized. They are produced by the reduction of a mixture of iron and manganese ores—or of manganese ore containing iron—with fuel in a blast-furnace; occasionally an electric furnace is used. It is desirable not to employ too high a temperature, owing to the volatility of manganese. The production of these alloys is discussed in the section on iron.

Small quantities of manganese are added to steel as a deoxidizer. Larger quantities are added to confer specific qualities on the metal, which is then known as *manganese steel*. Manganese steel possesses extraordinary toughness.

During the war, owing to the shortage of high-grade manganese ores, spiegeleisen was often used where the rich alloys (ferro-manganese) had been used before. In so far as manganese was required as a deoxidizer, the shortage was partly overcome by the substitution of other elements (titanium, etc.) which have an affinity for oxygen.

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[1] M. Haney, *Min. Ind.* 28 (1919), 442.

Manganese in Copper Alloys. Manganese is also a constituent of the alloy known as **manganese bronze**, which is really a brass containing manganese and usually iron and aluminium besides (see Vol. IV). In addition manganese is used in small quantities in other alloys of copper, such as nichrome, Monel metal and German silver, its main function being apparently that of a deoxidizer,[1] and possibly that of a desulphurizer also.

Certain copper-manganese alloys containing a larger proportion of manganese are used for special purposes. Copper containing 4–6 per cent. of manganese retains its strength remarkably well at high temperatures, and has been found very suitable for fire-box stays [2]; copper-manganese alloys have also been used for turbine blading.[3] The alloy known as **manganin**,[4] which contains about 82–84 per cent. copper, 12–15 per cent. of manganese, 2–4 per cent. of nickel, and 0–1 per cent. of iron, has some importance in the preparation of resistance coils, owing to the fact that the electrical resistance is almost independent of the temperature.

Permanganates as Oxidizing Agents. Several of the compounds of manganese have considerable industrial importance. In order to prepare **manganates** and **permanganates** from natural pyrolusite, the oxidizing action of the air is made use of. If, for instance, a mixture of sodium hydroxide and powdered pyrolusite is roasted for some days in a flat pan, the latter becomes largely converted to sodium manganate. By extraction with water, and subsequent treatment of the dark green liquid with carbon dioxide, a concentrated solution which contains permanganate as well as manganate is obtained. This solution has strong oxidizing and disinfecting properties, attacking organic bodies generally. The solution can be sold, without separation of the constituents, for use as a deodorizer and sterilizer.

Where a solid oxidizing agent is demanded, potassium permanganate is generally prepared, as this crystallizes better than the sodium salt. In that case caustic potash is heated with pyrolusite, and the aqueous extract from the product, which contains chiefly potassium manganate, is acidified either with sulphuric acid or with carbon dioxide, and then boiled. One-third of the manganate is reduced to manganese dioxide (or a manganite) and the rest is oxidized to a permanganate. The solution is filtered free from manganese dioxide, and evaporated; upon cooling it deposits crystals of potassium permanganate.

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[1] A. F. Braid, *Trans. Amer. Inst. Min. Eng.* **60** (1919), 371.

[2] E. F. Law, "Alloys and their Industrial Application" (Griffin).

[3] W. B. Parker, *J. Inst. Met.* **14** (1915), 53.

[4] M. A. Hunter and J. W. Bacon, *Trans. Amer. Electrochem. Soc.* **36** (1919), 323.

In the method just described one-third of the manganese returns to the state of dioxide and requires reoxidation. In some works, therefore, the oxidation of manganate to permanganate is carried out electrolytically. The manganate solution, without addition of acid, is introduced into the anode compartment of a cell divided by a porous diaphragm. The cathode compartment contains dilute alkali. Iron or nickel electrodes can be used, the anode becoming in each case quite passive. When a current passes the manganate becomes oxidized to permanganate round the anode; at the cathode hydrogen is evolved, and the alkali solution becomes more concentrated. Low anodic current density favours a high current efficiency, but even under the most favourable circumstances, a considerable fraction of the current is wasted upon oxygen-evolution.

In addition to its use as a deodorizer and disinfectant, potassium permanganate serves as the source of other manganese compounds; when reduced by sulphur dioxide in acid solution, manganous salts are obtained, whilst reduction in neutral solution yields forms of the dioxide which are more reactive than natural pyrolusite.

Manganese in Glass. Manganese dioxide is considerably used in the glass industry as a decolorizer. As already explained, its function is twofold. Firstly, it serves to oxidize the iron present from the ferrous to the ferric state, causing the deep green of the ferrous compounds to be replaced by the less intense yellow-green of the ferric compounds. Secondly, the violet colour of the manganic compounds produced serves to mask the yellow-green colour, being roughly complementary to it. Many kinds of native pyrolusite are quite suitable for use in the glass-batch. Manganese is also added in larger quantities both to glass and to glazes as a colouring matter; it confers a violet colour or a dark brown, according to the composition of the glass, the state of oxidation, and the amount added.

Manganese Dioxide in Primary Cells.[1] The oxidizing properties of manganese dioxide are also utilized in the Leclanché cell, the so-called "dry" form of which is now manufactured by the million, being used for electric torches, bells, telephones, and for "ignition" purposes. The word "dry" is really a misnomer, for if the cell were truly dry, it would be inactive. It contains, however, no free liquid, but merely a moist pasty mixture; the cell is thus available for transport without fear of spilling. A section of a dry cell is shown in Fig. 19. The manganese dioxide mixed with granulated carbon (usually both graphite and petroleum coke are used) is packed tightly round a carbon rod which forms the positive electrode; the mixture is contained in a zinc canister which forms the negative pole, but is kept from coming into actual contact with the zinc by a layer of absorbent paper, pulpboard, or, in some forms of cell, canvas. The whole is kept moist with a solution of ammonium chloride, often mixed with zinc chloride, as the zinc salt is found to reduce the local corrosion of the metallic zinc. Hygroscopic substances such as calcium chloride are also sometimes added to prevent any danger of the water evaporating altogether. Above the manganese dioxide mixture comes a layer of sand or sawdust, which acts as an expansion chamber for any gas which may be produced; the top of the cell is sealed with pitch.

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[1] C. M. Weld, *U.S. Bur. Mines, Bull.* 173 (1920), 16; D. L. Ordway, *Trans. Amer. Electrochem. Soc.* 17 (1910), 341.

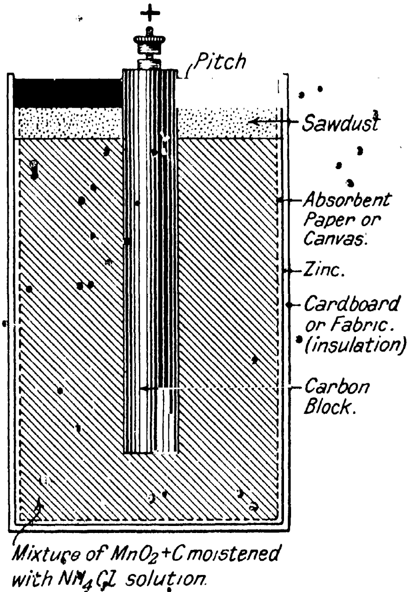
+
Pitch
Sawdust
Absorbent Paper or Canvas.
Zinc.
Cardboard or Fabric. (insulation)
Carbon Block.
Mixture of MnO_2+C moistened with NH_4Cl solution.

Fig. 19.—Dry Cell.

When the cell produces a current, the zinc enters the ionic state, forcing out hydrogen on to the granular carbon of the porous mixture, which hydrogen is quickly removed by interaction with the manganese dioxide. When fresh the cell should yield 1·5 volts, but if the cell is called upon to furnish a powerful current, hydrogen begins to accumulate on the carbon and the E.M.F. drops far below that value. In a good cell, however, the E.M.F. should recover quickly if the cell is allowed to rest; to ensure this it is clearly necessary that the manganese dioxide should be of a highly reactive variety.

Very much research work has been devoted to the study of the depolarizing behaviour of different forms of manganese dioxide. A slightly higher E.M.F. can be obtained by using artificial dioxide, but the natural pyrolusite is generally used by cell-makers. Up till the war, very pure pyrolusite from the Caucasus was generally employed; but when this supply was cut off, it was found possible to use material with 2–3 per cent. of iron, without loss of efficiency.[1] It is generally considered best to have the manganese dioxide in a fairly coarse, but porous, form, and to mix it with comparatively fine carbon, so that a conducting coat of carbon is formed over each grain of dioxide.

Innumerable patents have been taken out for special forms of artificial manganese dioxide—or mixtures containing the dioxide—designed for use as depolarizers in dry cells. As far as one can judge, the inventors appear to have been aiming at two separate goals; some have sought to obtain the dioxide in the most reactive form possible, and others to obtain it in the most conductive form possible. To some extent these two *desiderata* are irreconcilable, since high reactivity demands a porous form with large surface area, whilst high conductivity requires a compact material.

All the materials used in the cell must be free from elements like copper or arsenic, which, by producing local corrosion couples on the zinc surface, would cause the cell to deteriorate on keeping. For the same reason, it is important that the manganese dioxide and carbon should not include particles sufficiently small to pass through the porous layer, and come into contact with the zinc.

Even the best cells which can be produced under commercial conditions[2] do, however, deteriorate on keeping, especially in hot climates. Where cells are likely to be stored for some time before being used, the so-called "inert" type of cell is to be preferred. This type is truly dry, being quite free from moisture as it leaves the factory, and as long as it remains dry it cannot deteriorate. When actually required for use, water is poured in through a hole in the top, and is taken up by the materials within the cell. The cell is then moist and active, like the ordinary form of "dry cell," and is capable of yielding a current.

Manganese Compounds as "Driers."[3] Manganese compounds are frequently added to paints and varnishes as "driers." The drying of linseed and similar oils is partly an oxidation process, the oxygen of the air being absorbed into the film to form solid oxidized substances. The presence of a catalyst or "oxygen carrier" facilitates the process. As is usually the case, it is those metals which possess more than one stable oxide which are effective as oxygen-carriers; lead, cobalt and manganese salts have all been used as driers. **Manganese borate**, formed by precipitation, is still largely used for this purpose, as is also the **dioxide.** But organic salts like **manganous rosinate** and **manganous linoleate** have come into favour; they have the advantage of being soluble in the oils in question.

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[1] "Manganese, 1913–1919" (Imperial Mineral Resources Bureau), page 11.

[2] Compare F. Kainz, *Chem. Zeit.* 45 (1921), 602.

[3] See L. E. Andés, "Drying Oils, Boiled Oils and Solid and Liquid Driers" (Scott, Greenwood).

Manganese Pigments. One or two compounds of manganese have a value as pigments. **Barium manganate** (*Cassel green*) is a fine green powder, formed when the dioxide is heated with barium nitrate in air, but it is not much used now. A **hydrated dioxide** (*manganese brown*) is sometimes utilized as an inorganic colouring material in the dyeing of fabric. It is formed *in situ* in the following way. The fabric is steeped first in manganous sulphate, then in caustic soda; it is then washed and dried, the manganous hydroxide precipitated within it becoming oxidized on exposure to the air. The colour is not very satisfactory if used alone, but if other oxides (e.g. those of iron and chromium) are precipitated at the same time, quite fine tones are produced.

The **Umbers** are pigments made from certain naturally occurring iron-manganese hydroxide ores, which are ground, levigated where necessary, and then usually "burnt." Burnt umber is a cheap and permanent brown pigment of good covering power, and with careful burning, rich tones of brown can be obtained, which vary rather amongst ores of different origin. A fine quality of umber comes from Cyprus. Umber is also used in the raw (unburnt) state.

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ABRIDGED FORM OF PERIODIC TABLE.

O.	IA.	IIA.	IIIA.	IVA.	VA.	VIA.	VIIA.	Transition Elements.			IB.	IIB.	IIIB.	IVB.	VB.	VIB.	VIIB.	O.
2 He	3 Li	4 Be	5 B											6 C	7 N	8 O	9 F	10 Ne
10 Ne	11 Na	12 Mg	13 Al											14 Si	15 P	16 S	17 Cl	18 A
18 A	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 —	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
54 Xe	55 Cs	56 Ba	57 La	58 Ce														
			57–71 Rare Earth Metals															
					73 Ta	74 W	75 —	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 —	86 Nt
86 Nt	87 —	88 Ra	89 Ac	90 Th	91 UX_2	92 U												

See VOLUME II VOLUME III VOLUME IV of this work